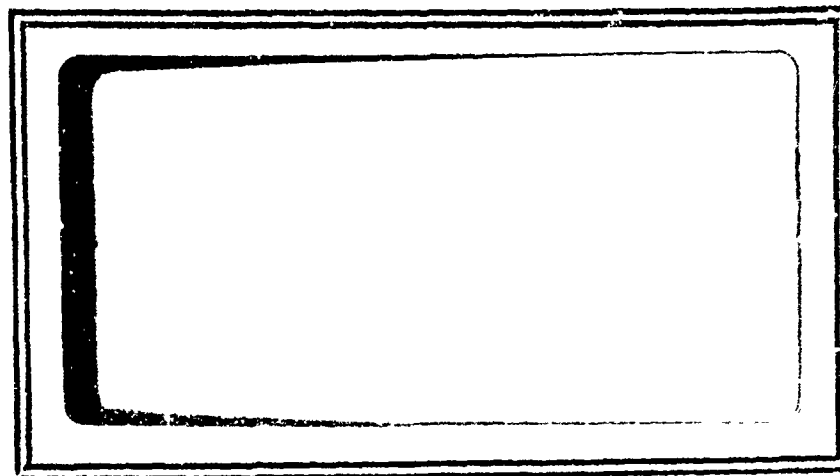
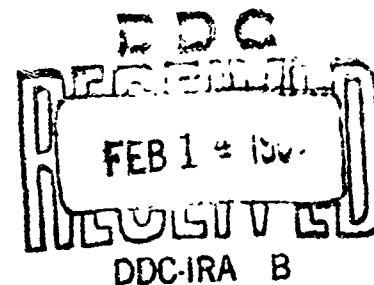


AD628961



CLEARINGHOUSE FOR FEDERAL SCIENTIFIC AND TECHNICAL INFORMATION		
Hardcopy	Microfilm	
\$ 8.60	\$ 0.75	82 ppas
ARCHIVE COPY		

Code 1



THE ELECTRIC STORAGE BATTERY CO.

THE CARL F. NORBERG RESEARCH CENTER

YARDLEY, PENNA.

AD

TECHNICAL REPORT ECOM-01394-1  
HIGH ENERGY SYSTEM (ORGANIC ELECTROLYTE)

FIRST QUARTERLY REPORT

By

D. P. BODEN, H. R. BUHNER, V. J. SPERA

OCTOBER 1965

ECOM

UNITED STATES ARMY ELECTRONICS COMMAND • FORT MONMOUTH, N. J.

CONTRACT DA-28-043-AMC-01394(E)

THE ELECTRIC STORAGE BATTERY COMPANY  
THE CARL F. NORBERG RESEARCH CENTER  
YARDLEY, PENNSYLVANIA

TECHNICAL REPORT ECOM-01394-1

OCTOBER 1965

HIGH ENERGY SYSTEM (ORGANIC ELECTROLYTE)

FIRST QUARTERLY REPORT

15 June 1965 To 15 September 1965

Report No. 1

CONTRACT NO. DA-28-043-AMC-01394(E)

Prepared by

D. P. BODEN, H. R. BUHNER, V. J. SPERA

THE ELECTRIC STORAGE BATTERY COMPANY  
THE CARL F. NORBERG RESEARCH CENTER  
YARDLEY, PENNSYLVANIA

For

U. S. ARMY ELECTRONICS COMMAND, FORT MONMOUTH, N. J.

## ABSTRACT

The study of high energy density systems in the first quarter included conductance measurements of various non-aqueous electrolytes; corrosion and solubility studies of electrode materials in electrolytes; preparation of a reversible lithium reference electrode; fabrication and evaluation of lithium anodes and  $\text{CuF}_2$ ,  $\text{CoF}_3$  and  $\text{CrF}_3$  cathodes; thermodynamic studies of the lithium-cupric fluoride cell; and kinetic studies of the cupric fluoride discharge reaction.

Conductance measurements revealed maxima of specific conductance with approximately 1 Formal solution for the majority of electrolytes tested. Further, for  $\text{LiClO}_4$  in propylene carbonate, it was shown that the electrolyte was completely dissociated into ions which were essentially unsolvated.

Corrosion and solubility studies revealed an optimum compatibility for the couple  $\text{Li-CuF}_2$  in  $\text{LiClO}_4$  in propylene carbonate electrolyte.

A hot-pressing technique was evolved as the best method of fabricating cathodes, and  $\text{CuF}_2$  was found to be the best cathode material. A utilization of 55 - 60 % of the  $\text{CuF}_2$  in an electrode was obtained with a current density of  $1.6 \text{ ma/cm}^2$ , when discharged in 1 Formal  $\text{LiClO}_4$  in propylene carbonate.

A lithium anode with good performance was obtained by simply pressing lithium foil on a copper grid. An electrode of this type was 70-75% efficient when discharged as described above for the  $\text{CuF}_2$  cathode.

Values of  $\Delta G$   $25^\circ\text{C}$  of -164.3 kcal and -162.5 kcal were obtained for the reaction  $2\text{Li} + \text{CuF}_2 \rightarrow 2\text{LiF} + \text{Cu}$ , based on cell voltage measurements of a  $\text{Li-CuF}_2$  cell. These values agree to within 1/2% with literature values for the stated reactions.

A study of the kinetics of the  $\text{CuF}_2$  discharge reaction indicated that a two-electron charge may be involved, i.e.,  $\text{CuF}_2 + 2e \rightarrow \text{Cu} + 2\text{F}^{-1}$ , rather than a two step process such as (1)  $\text{CuF}_2 + 1e \rightarrow \text{CuF} + \text{F}^{-1}$  and (2)  $\text{CuF} + 1e \rightarrow \text{Cu} + \text{F}^{-1}$ .

The  $\text{Li/Li}^+$  electrode was found to behave reversibly. However, a method must be found to prevent deposition of soluble cathode materials on the lithium, with consequent voltage fluctuation, before it can be used reliably to measure cathode potentials.

## TABLE OF CONTENTS

Abstract . . . . .	i
List of Tables . . . . .	ii
List of Figures . . . . .	iii
Introduction . . . . .	1
Experimental . . . . .	2
1. Electrolyte Studies . . . . .	2
1.1 Screening Tests . . . . .	2
1.1.1 Purification of Material . . . . .	2
1.1.2 Determination of Specific Conductances . . . . .	3
1.2 Conductance of $\text{LiClO}_4$ in Propylene Carbonate . . . . .	3
1.2.1 Purification of Materials . . . . .	3
1.2.2 Determination of Conductance . . . . .	3
1.2.3 Use of Fuoss-Accascina Equation . . . . .	6
2. Corrosion and Solubility Studies - Cathode and Anode Materials. . . . .	8
3. Reference Electrodes . . . . .	9
3.1 Preparation of Lithium Reference Electrodes . . . . .	9
3.2 Determination of Reversibility. . . . .	9
3.3 Measurement of Cell Potential . . . . .	10
4. Cathode Studies . . . . .	11
4.1 Cupric Fluoride Cathodes . . . . .	11
4.1.1 Pasted Electrodes. . . . .	11
4.1.1.1 Experimental Procedure . . . . .	12
4.1.1.2 Method of Preparation . . . . .	13
4.1.1.3 Electrode Testing . . . . .	13
4.1.1.4 Results of Statistical Analysis. . . . .	14
4.1.2 Hot Pressed $\text{CuF}_2$ Cathodes . . . . .	17
4.1.2.1 Factorial Statistical Analysis of Preparation Parameters . . . . .	17
4.1.2.2 Effect of Compacting Pressure on Performance . . . . .	18
4.1.2.3 Effect of Graphite on Performance . . . . .	19
4.1.2.4 Effect of Amount of Binder on Performance . . . . .	19
4.1.2.5 Effect of Particle Size of $\text{CuF}_2$ on Performance . . . . .	20

## TABLE OF CONTENTS (cont'd)

4.1.2.6	Discharge in 1 Normal $\text{LiClO}_4$ in Dimethyl Sulphoxide . . . . .	20
4.1.2.7	Substitution of Lampblack for Graphite . . . . .	21
4.1.3	Pressed Cylindrical Electrodes . . . . .	21
4.1.4	Electroformed $\text{CuF}_2$ Cathodes . . . . .	22
4.2	Cobalt Trifluoride Cathodes . . . . .	23
4.3	Chromium Trifluoride Cathode . . . . .	23
5.	Thermodynamic Studies - Li - $\text{CuF}_2$ Cell . . . . .	23
5.1	Experimental Procedure. . . . .	23
5.2	Results and Discussion . . . . .	24
6.	Effect of Current Density on Performance of $\text{CuF}_2$ Electrodes . . . . .	25
6.1	X-Ray Diffraction Studies . . . . .	26
7.	Lithium Electrode Studies . . . . .	27
7.1	Pressed Foil Electrodes. . . . .	27
	References . . . . .	29

## LIST OF TABLES

- 1        **Energy density of conventional systems**
- 2        **Estimated future performance of presently available cells**
- 3        **Physico-chemical properties of anode materials**
- 4        **Physico-chemical properties of cathode materials**
- 5        **E.M.F and energy densities of various couples**
- 6        **Physico-chemical properties of non-aqueous solvents**
- 7        **Conductance of  $\text{LiClO}_4$  in propylene carbonate solutions**
- 8        **Viscosity and density of  $\text{LiClO}_4$  in propylene carbonate**
- 9        **Comparison of observed and calculated conductances -  $\text{LiClO}_4$  - propylene carbonate**
- 10       **Solubility of cathode materials in electrolyte**
- 11       **Variation of potential of Li electrode with concentration of electrolyte**
- 12       **Liquid junction potential**
- 13       **Statistical factorial analyses - pasted  $\text{CuF}_2$  cathodes**
- 14       **Analyses of variance**
- 15       **Effect of amount of graphite and compacting pressure on performance -  $\text{CuF}_2$  cathode**
- 16       **Statistical factorial analysis - hot-pressed  $\text{CuF}_2$  cathodes**
- 17       **Thermodynamic properties of Li- $\text{CuF}_2$  cell reaction**

## LIST OF FIGURES

### Figure

- 1-4 Specific conductance of non-aqueous electrolytes
- 5 Shedlovsky extrapolation function
- 6 Determination of  $\Lambda_0$  and J for  $\text{LiClO}_4$  in propylene carbonate
- 7 Determination of  $A^\circ$  from  $J(A)$
- 8 Gas evolution pipet
- 9 Lithium gassing tests
- 10 Reference electrode cell
- 11 E.M.F. vs.  $\text{Log } C_2$  - Lithium reference electrode
- 12 Typical discharge characteristic - pasted  $\text{CuF}_2$  electrode
- 13 Effect of compacting pressure on performance of  $\text{CuF}_2$  cathodes
- 14 Discharge efficiency vs. compacting pressure -  $\text{CuF}_2$  cathodes
- 15 Effect of graphite concentration on performance of  $\text{CuF}_2$  cathodes
- 16 Effect of amount of binder on performance of  $\text{CuF}_2$  cathodes
- 17 Effect of particle size of  $\text{CuF}_2$  on cathode performance
- 18 Performance of  $\text{CuF}_2$  cathodes in dimethyl sulphoxide -  $\text{LiClO}_4$
- 19 Effect of carbon filler on performance of  $\text{CuF}_2$  cathodes
- 20 Performance of cylindrical  $\text{CuF}_2$  cathodes
- 21 Performance of  $\text{CoF}_3$  and  $\text{CrF}_3$  cathodes
- 22 Cell voltage vs. temperature -  $\text{Li-CuF}_2$  cell
- 23  $\Delta G$  vs. temperature  $\text{Li-CuF}_2$  cell
- 24 Electrode test cell
- 25 Effect of current density on performance of  $\text{CuF}_2$  cathodes



LIST OF FIGURES (cont'd)

Figure

- 26 Polarization vs. current density -  $\text{CuF}_2$  cathodes
- 27 Kinetic study -  $\text{CuF}_2$  cathodes
- 28 Typical discharge characteristics of lithium foil anodes

## INTRODUCTION

The necessity of developing high energy density systems has increased during the last decade due to the increasing power requirements of modern military equipment. Conventional aqueous batteries are unable to meet these demands, having energy densities that are generally too low. For example the theoretical and practical energy densities of several conventional systems is shown in Table I <sup>(1)</sup>.

The estimated future performance <sup>(1)</sup> of some presently available cells is shown in Table 2.

Clearly the projected energy densities of the systems shown in Table 2 would be necessary to give a battery of output greater than 200 W-hr/lb.

Future predictions indicate little possibility of significant improvement for these couples.

The voltage of a galvanic cell is given by

$$E^{\circ} = \frac{-\Delta F^{\circ}}{n F}$$

where  $\Delta F^{\circ}$  is the standard free energy change of the reaction

$F$  is the Faraday constant

$n$  is the number of equivalents of electricity flowing per mole of reaction.

Thus, the greater the negative value of the free energy the greater will be the cell voltage.

Further, the most desirable cell reaction would be one where the sum of the free energies of the reactants have a low negative value and the sum of the free energies of the products have a large negative value. The anode materials which most generally obey the above criteria are the metals of the alkali and alkali earth series. Table 3 shows some physico-chemical properties of various anode metals.

Of the metals shown in Table 3 lithium appears to be outstanding as a potential high energy anode. Among the most attractive cathode materials are the fluorides of the low atomic weight transition metals. Table shows some physico-chemical properties of potential cathode materials <sup>(2)</sup>.

The E.M.F. and energy density of couples formed from these cathode salts with lithium can now be calculated and are shown in Table 5.

On the basis of the calculations in Table 5 lithium was selected as the anode and it was decided to investigate  $\text{CuF}_2$ ,  $\text{CoF}_3$ , and  $\text{CrF}_3$  as potential cathode materials.

## EXPERIMENTAL

### 1. Electrolyte Studies

The electrolyte for any kind of galvanic cell whether aqueous or non-aqueous must possess certain physical and chemical properties. First, the electrolyte should be highly conducting. It should have a wide liquid range, low density and viscosity and a low vapor pressure.

The ability of a solvent to dissolve and ionize a salt to give a conducting solution depends to a large extent on its dielectric constant. If the dielectric constant is low, association of the ions into non-conducting pairs or triplets will be encouraged with consequent loss in conductance. Since the conductance of an electrolytic solution is a measure of the rate at which the ions migrate under the influence of an electric field, frictional forces, that is the viscosity of the solution, play an important part. In order to achieve the highest mobility the viscosity should preferably be low. The conductance is also influenced by the size of the migrating ion which in turn will depend on whether the ion is complexed or not, the degree of solvation and of course the crystallographic radius.

If the density of the electrolyte is high, this will result in too much dead weight in the cell with consequent reduction in energy density. The melting point and boiling point of the electrolyte are important in that they define the useful working temperature range of the cell and the vapor pressure should be low in order to minimize loss of solvent by evaporation during long storage periods.

A number of solvents which had all or some of the above properties were selected for evaluation. Table 6 shows some of the solvents selected with their relevant physico-chemical properties.

The solutes studied with the above solvents were  $\text{KCNS}$ ,  $\text{NH}_4\text{CNS}$ ,  $\text{AlCl}_3$ ,  $\text{LiCl}$ ,  $\text{KPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiBr}$  and  $\text{ZnCl}_2$ .

### 1.1 Screening Tests

#### 1.1.1 Purification of Materials

All the solvents used were the purest commercially available and were dried by standing for one week over Linde No. 5A molecular sieve or  $\text{CaO}$ . The solutes were dried in a vacuum oven at  $100^\circ\text{C}$  with the exception of  $\text{AlCl}_3$  which was purified by sublimation in dry nitrogen.

### 1.1.2 Determination of Specific Conductance

All solutions were prepared in a glove box under an atmosphere of dry nitrogen. The conductance was measured at 25°C at a frequency of 1000 c.p.s. in a cell of constant 0.134 for dilute solutions or a cell of constant 0.926 for solutions of higher conductance. The bridge was either an E.S.1 Universal Impedance Bridge, Model 291 or a Wayne Kerr Universal Bridge Model 221.

The results of the conductance measurements are shown in Figures 1, 2, 3 and 4.

An interesting feature of the curves is the maximum in the specific conductance which for the majority of the electrolytes studied lies around 1 Formal. For lithium bromide the maximum is found at 0.5 Formal. The position of the maximum is largely independent of the solvent for example, the maxima for lithium perchlorate solutions occur at 1.0 Formal in propylene carbonate, acetonitrile, dimethyl formamide and dimethyl sulfoxide; solvents which have widely differing physical properties. The maximum may be due to the increasing viscosity of the solutions as solute is added. The specific conductance values generally lie in the same order of solute irrespective of the solvent. It is observed that the values for propylene carbonate solutions are quite low compared to the other solvents in spite of its high dielectric constant. This can be attributed to its high viscosity which will reduce the mobility of the ions.

Corrosion and solubility screening tests (See Section 2) had indicated that only propylene carbonate and dimethyl sulfoxide were suitable for electrolytes, the other solvents either attacked the lithium or dissolved the cathode. It was decided, therefore, to examine these electrolytes more closely to determine the factors affecting the conductance. The first experiments were carried out with solutions of  $\text{LiClO}_4$  in propylene carbonate.

## 1.2 Conductance of $\text{LiClO}_4$ in Propylene Carbonate

### 1.2.1 Purification of Materials

The  $\text{LiClO}_4$  was purchased from G. Frederick Smith and Co., Columbus, Ohio and was dried at 120°C under a pressure of 2mm Hg for 16 hours. Propylene carbonate was Eastman Organic Chemical Co. practical grade which was dried over Linde No. 5A molecular sieve and twice distilled at reduced pressure (2mm Hg), a middle cut being taken each time. Approximately 25% of the solvent was discarded at the beginning and end of each distillation. The measured specific conductance of the twice distilled propylene carbonate was  $2.3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The solutions were prepared from a stock solution of 0.01 and 1.00 Formal under dry nitrogen.

### 1.2.2 Determination of Conductance

The conductance was determined as described previously. The results are shown in Table 7.

The values of the equivalent conductance are much lower than those obtained from aqueous solutions. Another interesting feature is the rapid drop in conductance as the ionic strength is increased.

The equivalent conductance at infinite dilution can now be determined by use of the Shedlovsky extrapolation function (3).

If the Onsager equation is written in the following manner

$$\Lambda = \Lambda_0 - (\alpha \Lambda_0 + \beta) C^{1/2} \quad (1)$$

and solved for  $\Lambda_0$  the result is

$$\Lambda_0' = (\Lambda + \beta C^{1/2}) / (1 - \alpha C^{1/2}) \quad (2)$$

Shedlovsky showed that  $\Lambda_0'$  is linear in concentration so if  $\Lambda_0'$  is computed and plotted against  $C$ , a straight line is obtained which can be extrapolated to zero to give the true value of  $\Lambda_0$ . This is a much more accurate method than simply extrapolating conductance curves.

For propylene carbonate at 25°C

$$\alpha = \frac{8.204 \times 10^5}{(DT)^{3/2}} \quad \text{and} \quad \beta = \frac{82.501}{\eta (DT)^{1/2}}$$

where  $D$  is the dielectric constant and  $T$  is the absolute temperature. The dielectric constant of propylene carbonate is 64.4 (4). Thus at 25°C

$$\alpha = 0.3084 \quad \text{and} \quad \beta = 29.62$$

$\Lambda_0'$  was computed and plotted against concentration as shown in Figure 5. A straight line is obtained which extrapolates to  $\Lambda_0 = 26.39$ . This compares to  $\Lambda_0 = 105.98$  in water.

The low value of the equivalent conductance is most likely due to the high viscosity of the solutions since the dielectric constant is sufficiently high to preclude extensive ion association.

To test the above hypothesis the viscosity of the electrolyte was determined using an Ostwald viscometer calibrated with twice distilled water at 25°C. The results are shown in Table 8.

It has been shown that extensions to the theory of Onsager (5) to include the effect of finite ion sizes gives an equation for the conductance of a 1:1 electrolyte of the form.

$$\Lambda = \left( \Lambda^\circ - \frac{82.5}{(\text{DT})^{1/2}} \frac{C^{1/2}}{1 + K\alpha} \right) \left( 1 + \frac{\Delta x}{x} \right) \quad (3)$$

where

$$\frac{\Delta x}{x} = \frac{-e^2}{3 \text{DKT}} \cdot \frac{0.2929 K}{1 + K\alpha} \times \frac{e^{0.2929 K\alpha - 1}}{0.2929 K\alpha} \quad \text{and}$$

$$K = \left( \frac{8 \pi N e^2}{1000 \text{DKT}} \right)^{1/2} C^{1/2}$$

where the symbols have their usual meaning. Combining the above equations gives

$$\Lambda = \left( \Lambda^\circ - \frac{\beta_2 C^{1/2}}{1 + \beta_1 \alpha^\circ C^{1/2}} \right) \left( 1 - \frac{\beta_1 C^{1/2}}{1 + \beta_1 \alpha^\circ C^{1/2}} \times F \right) \quad (4)$$

where  $\beta_1 = \frac{8.20 \times 10^5}{(\text{DT})^{3/2}} = 0.3084$

$$\beta_2 = \frac{82.5}{\eta (\text{DT})^{1/2}} = 29.62$$

$$\beta_1 \alpha^\circ C^{1/2} = \frac{50.29 \alpha^\circ C^{1/2}}{(\text{DT})^{1/2}} = K\alpha$$

$$F = \frac{e^{0.2929 K\alpha - 1}}{0.2929 K\alpha}$$

The only adjustable parameter in equation (4) is  $\alpha^\circ$  the distance of closest approach of the ions.

This equation modified by the relative viscosity to give

$$\Lambda_{\eta} = \left[ \Lambda_0 - \frac{\beta_2 C^{1/2}}{1 + \beta \alpha^{\circ} C^{1/2}} \right] \left[ 1 - \frac{\beta_1 C^{1/2}}{1 + \beta \alpha^{\circ} C^{1/2}} F \right] \frac{\eta^{\circ}}{\eta} \quad (5)$$

has been used by Wishaw and Stokes (6) to explain the observed conductance of ammonium chloride solutions in water and by Dunnett and Gasser (7) to explain the conductance of LiCl in dimethyl sulphoxide.

By assigning different values to  $\alpha^{\circ}$  a series of conductance curves was computed and compared to the experimental results. The computed values are given in Table 9.

The computed values of  $\Lambda_{\eta}$  do not fit the experimental values, significant deviations occurring at high concentrations. On examination of the calculated values of  $\Lambda$  it can be seen that a fairly close fit to the experimental points is obtained when  $\alpha^{\circ} = 2.0$  angstroms. It would appear, therefore, that the effect of increasing viscosity due to addition of solute is not a determining parameter of the conductance function.

The distance of closest approach can be regarded as the sum of the radii of the ions which in turn depends upon their degree of solvation. The crystallographic radius of the  $\text{Li}^+$  ion is 0.60 angstroms and the radius of the  $\text{ClO}_4^-$  ion has been given as 1.36 angstroms (8) which would give a distance of closest approach of 1.96 angstroms. The close agreement between this value and that found from the conductance equation indicates that the ions are not solvated by the propylene carbonate.

### 1.2.3 Use of the Fuoss-Accascina Equation

The conductance function used above is not very sensitive to changes in  $\alpha^{\circ}$  and thus the value obtained can only be regarded as approximate. Recently, an extended form of the conductance equation has been derived (9) which allows ion parameters to be determined with greater precision. This has the form

$$\Lambda = \Lambda_0 - SC^{1/2} + EC \log C + JC - F \Lambda_0 C \quad (6)$$

where

$$S = \alpha \Lambda_0 + \beta = 0.3084 \Lambda_0 + 29.62$$

$$E = \frac{6.7747 \times 10^{12} \Lambda_0}{D^3 T^3} - \frac{0.9977 \times 10^8}{\eta D^2 T^2}$$

$$J = \sigma^1 \Lambda_0 + \sigma_2$$

$$\sigma^1 = \frac{K^2 a^2 b^2}{12C} \left[ h(b) + 0.9074 + \ln \left( \frac{Ka}{C^{1/2}} \right) \right]$$

$$\sigma_a = a\beta + \frac{11\beta Ka}{12 C^{1/2}} - \frac{Kab\beta}{8 C^{1/2}} \left[ 1.0170 + \ln \left( \frac{Ka}{C^{1/2}} \right) \right]$$

$$F = \frac{\pi N R^3}{300} = 6.308 \times 10^{21} R^3$$

$$h(b) = \frac{2b^2 + 2b - 1}{b^3}$$

where C = concentration

a = distance of closest approach of the ions

$$b = \frac{e^2}{aDKT}$$

k = Boltzmann constant

e = electronic charge

R = hydrodynamic radius

For  $\text{LiClO}_4$  in propylene carbonate at  $25^\circ\text{C}$

$$S = 37.761 \text{ and } E = 12.09$$

For small ions F can be neglected and equation (6) becomes

$$\Lambda = \Lambda_0 - 37.761 C^{1/2} + 12.09 C \log C + JC$$

rearranging

$$\Lambda_0 + JC = \Lambda_1 = \Lambda + 37.761 C^{1/2} - 12.09 C \log C$$

$\Lambda_1$  can be computed and plotted against concentration to evaluate  $\Lambda_0$  and J. This has been done in Figure 6. A value of 26.38 is found for  $\Lambda_0$  and J equals 47.945.

The equation

$$J = \frac{K^2 a^2 b^3 \Lambda}{12 C} \left( h(b) + 0.9074 + \ln \frac{Ka}{C^{1/2}} \right) + a\beta + \frac{11\beta Ka}{12 C^{1/2}} - \frac{Kab\beta}{8 C^{1/2}} \left( 1.0170 + \ln \frac{Ka}{C^{1/2}} \right)$$



$$= 0.8277 A_0 \left( h(b) + \ln a^\circ - 0.10595 \right) + 9.137 + 9.854 a^\circ - 11.69 \left( \ln a^\circ + 0.00365 \right)$$

was used to compute J as a function of a giving

J (4.0)	=	87.1559
J (3.0)	=	66.8395
J (2.5)	=	56.3425
J (2.0)	=	45.6467

A plot of J vs.  $a^\circ$  is shown in Figure 7. The plot is beautifully linear, thus allowing  $a^\circ$  to be interpolated. The value of  $a^\circ$  corresponding to the observed value of J is 2.1 angstroms which is in excellent agreement with the expected value of 1.96. This confirms the conclusion that solvation is very slight.

In summary, we can regard a solution of  $\text{LiClO}_4$  in propylene carbonate to be completely dissociated into ions which are essentially unsolvated. The low conductance of the solution is due to the high viscosity of the solvent rather than the increasing viscosity due to the addition of ions.

## 2. Corrosion and Solubility Studies - Cathode and Anode Materials

In order to realize the maximum capabilities of a high energy density couple, it is necessary:

(1) The cathode material be insoluble in the electrolyte. Further, it must not be reactive with the electrolyte. Any solubility of the cathode material will result in self-discharge of the cell, since the cation of the cathodic material will be reduced at the anode.

(2) The anode must be resistant to attack by the electrolyte. The anode metal may corrode by either or both of the following processes:

(a) If the decomposition potential of the electrolyte solvent is low with respect to the anode potential, and

(b) By reaction with the solute of the electrolyte. Experiments were designed to test the solubilities of  $\text{CuF}_2$ ,  $\text{CoF}_3$ , and  $\text{CrF}_3$  cathode materials in various non-aqueous electrolytes. Two grams of each of the cathode materials were immersed in twenty-five ml of anhydrous electrolyte at  $30^\circ\text{C}$  in closed test tubes and shaken for four days. Since a large number of samples were involved the solubility was estimated by visual inspection.

The qualitative results are shown in Table 10. In general all the cathode salts were soluble to some degree in the electrolytes investigated. The least solubility was observed in  $\text{LiClO}_4$  solution in propylene carbonate, dimethyl formamide and acetonitrile. A more precisely constructed experiment will be carried out in the next quarter to determine the exact solubility of the above salts.

A convenient method of determining the rate of attack of an electrolyte on lithium is to measure the rate of gas evolution when the metal is immersed in a solution. Gassing tests were carried out in the pipets shown in Figure 8. A piece of lithium ribbon lin. x 1/4 in. x 1/16 in. was cleaned and placed in the cell. The cell was filled with electrolyte and the top inserted so as to expel all the air. The cell was maintained at 30°C, the rate of gas evolution being determined by the displacement of the meniscus. The results are shown in Figure 9.

Results of corrosion and solubility tests revealed optimum compatibility for lithium and cupric fluoride electrode materials in electrolytes of  $\text{LiClO}_4$  in propylene carbonate and  $\text{LiClO}_4$  in dimethyl sulphoxide. Performance of the cupric fluoride cathode, however, was found to be unsatisfactory in dimethyl sulphoxide -  $\text{LiClO}_4$  solutions (section 4), and consequently most of the half cell discharges described in this report were conducted in  $\text{LiClO}_4$  in propylene carbonate.

### 3. Reference Electrodes

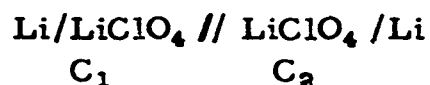
A study was initiated to investigate the possibility of developing suitable reference electrodes for non-aqueous electrolytes. It was decided to investigate electrodes for reversibility to the ions in the electrolyte presently being used so that the reference electrode could be placed directly in the cell thus avoiding the use of a salt bridge with consequent liquid junction potential. The electrolyte most often used in evaluating electrodes was 1 Formal  $\text{LiClO}_4$  in propylene carbonate. We decided, therefore, to investigate first the  $\text{Li}/\text{Li}^+$  electrode.

#### 3.1 Preparation of Lithium Reference Electrodes

The electrodes were prepared in a standard electrode cell (Figure 10). Lithium powder dispersion in Hexane was packed around the platinum contact wire and tamped down with a glass rod. A glass fibre pad was then packed into the end of the opening to keep the lithium powder in place. The electrodes were then leached free of hexane in twice distilled propylene carbonate for one week. Preparation and storage was carried out in a glove box filled with dry argon. This type of construction, except using  $\text{Ag}/\text{AgCl}$  material, was used as a reference electrode in most of the half cell cathode discharges described herein.

#### 3.2 Determination of Reversibility

The variation of potential of the reference electrode with concentration of  $\text{Li}^+$  was determined in the cell



The salt bridge was  $\text{LiClO}_4$  of concentration  $C_1$ .

The E.M.F. of the cell is given by

$$E_{\text{cell Li}^+/\text{Li}} = E^\circ_{\text{Li}^+/\text{Li}} - \frac{RT}{F} \ln \frac{a_{\text{Li}_2}}{a_{\text{Li}_1}^+} - \left( E^\circ_{\text{Li}^+/\text{Li}} - \frac{RT}{F} \ln \frac{a_{\text{Li}}}{a_{\text{Li}_1}^+} \right) + E_j$$

where  $E_j$  is the liquid junction potential and the subscript 1 and 2 refer to concentrations  $C_1$  and  $C_2$  respectively.

If  $a_{\text{Li}} = 1$

$$E_{\text{cell}} = \frac{RT}{F} \ln a_{\text{Li}_2^+} - \frac{RT}{F} \ln \text{Li}_1^+ + E_j$$

$$E_{\text{cell}} = \frac{RT}{F} \ln \frac{a_{\text{Li}_2^+}}{a_{\text{Li}_1^+}} + E_j$$

Replacing  $a$  by  $\gamma c$  where  $\gamma$  is the activity coefficient and  $c$  is the concentration.

$$E_{\text{cell}} = \frac{RT}{F} \ln \frac{\gamma_{\text{Li}_2^+}}{\gamma_{\text{Li}_1^+}} + \frac{RT}{F} \ln \frac{C_{\text{Li}_2^+}}{C_{\text{Li}_1^+}} + E_j$$

and if the activity coefficient ratio is unity

$$E = \frac{RT}{F} \ln \frac{C_{\text{Li}_2^+}}{C_{\text{Li}_1^+}} + E_j = 0.0591 \log \frac{C_{\text{Li}_2^+}}{C_{\text{Li}_1^+}} + E_j \text{ at } 25^\circ\text{C.}$$

If the concentration in one side of the cell is held constant while the other is varied, a change in potential of 0.0591 volts per tenfold concentration change should be observed if the electrode is reversible.

### 3.3 Measurement of Cell Potential

Solutions of  $\text{LiClO}_4$  in doubly distilled propylene carbonate were prepared in the concentration range 0.1 to 1.0 Formal. The concentration of the electrolyte in the left hand side of the cell ( $C_1$ ) and the salt bridge was held constant at 0.5 Formal, while the concentration of  $\text{LiClO}_4$  in the right hand side was varied in 0.1 Formal steps from 0.1 to 1.0 Formal. The potential was measured with a Rubicon Instruments potentiometer Model No. 2780S in conjunction with an optical galvanometer.

The results are shown in Table 11.

The liquid junction potential can be calculated by use of the Henderson-Planck equation

$$E_j = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2) \ln \frac{(U_1^1 + V_1^1)}{(U_1^1 + V_2^1)}}{(U_1^1 + V_1^1) - (U_1^1 + V_2^1)}$$

where  $U = \sum c + \lambda_+^0$  and  $V = \sum c - \lambda_-^0$  for the cations and anions in the end solutions indicated by the subscripts 1 and 2;  $U^1 = \sum c + \lambda_+^0 |Z_+|$  and  $V^1 = \sum c - \lambda_-^0 |Z_-|$ . Where  $|Z|$  is the valence of the ion.

The limiting ionic conductances have not been determined in propylene carbonate but a value for  $\text{Li}^+$  has been obtained in DMSO solutions (7). If we assume that  $\lambda_{\text{Li}^+}^0$  is the same in propylene carbonate and dimethyl sulphoxide, this value can be used to obtain  $\lambda_{\text{ClO}_4^-}^0$  in propylene carbonate.

The value given for  $\text{Li}^+$  is 11.4 which leads to a value of 15.00 for the perchlorate ion. Using these values the Henderson-Planck equation was solved for  $E_j$ . The results are shown in Table 12 together with the corrected cell E.M.F.

Figure 11 shows a plot of corrected potential against  $\log C_2$  for the cell. A slope of 0.057 volts is obtained which regarding the assumptions made in calculating the liquid junction potential is remarkably close to the expected result of 0.0591. We can conclude that the lithium electrode is reversible in propylene carbonate containing  $\text{LiClO}_4$ .

Lithium electrodes were used to determine electrode potentials but a disturbing feature soon became apparent. After several days of use, random fluctuations were observed in the potential together with differences in potential of up to 0.5 volt between pairs of identical electrodes. This phenomenon has not yet been explained but is most likely due to deposition of copper by galvanic exchange during measurements on  $\text{CuF}_2$  electrodes, since these are slightly soluble in the electrolyte. This problem will be further investigated during the next quarter.

#### 4. Cathode Studies

##### 4.1 Cupric Fluoride Cathodes

The initial phase of the program was an investigation of various fabrication techniques to produce high performance electrodes. Since cupric fluoride is a poor conductor of electricity, it was recognized that a conducting filler would be a necessary component of the electrode. The obvious choice was graphite because of its favorable low density. A binder is also necessary to achieve mechanical strength, and a suitable current collector which can also serve to improve strength. A number of techniques were investigated.

##### 4.1.1 Pasted Electrodes

A  $2^4$  factorial experiment was chosen for evaluation of the following parameters believed to affect cathode performance:

### (i) Particle Size of $\text{CuF}_2$ Powder

The rate and extent of reaction of the active material in the electrode structure are believed to be affected by the total surface area. Therefore, the particle size, and consequently the surface area, should be an important factor in performance.

### (ii) Conducting Matrix

Because of the high resistivity of  $\text{CuF}_2$ , it must be dispersed in an electrically conductive matrix in order to reduce resistive polarization to a minimum. This was done by mixing the  $\text{CuF}_2$  with graphite powder.

### (iii) Binder

A binder is required since compacting alone will not produce sufficient structural integrity. The binder chosen must not react with  $\text{CuF}_2$ , and the amount used should be small enough, consistent with good bonding characteristics, to avoid masking a large portion of the active surface. Polystyrene was chosen as a binder in this study.

### (iv) Compacting Pressure

The pore size and conductivity of the porous structure, as well as structural strength, were believed to be functions of compacting pressure.

The levels chosen for examination of the four factors were as follows:

<u>Factor</u>	<u>Level Low</u>	<u>Level High</u>
(a) Mesh size $\text{CuF}_2$	-170 + 325 mesh	-325 mesh
(b) Amount graphite	5%	10%
(c) Amount binder	1%	2%
(d) Compacting pressure	500 lbs/cm <sup>2</sup>	1000 lbs/cm <sup>2</sup>

Experiments were carried out in duplicate, involving a total of thirty-two electrodes.

#### 4.1.1.1 Experimental Procedure

The following materials were used in the fabrication of the pasted electrodes.

(1) $\text{CuF}_2$ (anhydrous) powder	Ozark-Mahoning Co.
(2) Graphite Powder	Southwestern-type 1651
(3) Polystyrene powder	Koppers Co.
(4) Carbon Tetrachloride (Reagent grade)	Fisher Scientific Co.
(5) Lithium Perchlorate (anhydrous)	G. F. Smith Co.
(6) Propylene Carbonate (Practical grade)	Eastman Organic Chemicals
(7) Expanded silver metal	Exmet Corp.

#### 4.1.1.2 Method of Preparation

(1)  $\text{CuF}_2$  and graphite powders, in the prescribed weight ratios, were thoroughly mixed in a Fisher-Kendall mixer for 16 hours.

(2) A solution of 5 grams of polystyrene in 150 ml of carbon tetrachloride was prepared. A specified volume was added to the  $\text{CuF}_2$  - graphite blend, and after thorough mixing the carbon tetrachloride was removed under vacuum.

(3) The final paste formulation was made by mixing the  $\text{CuF}_2$ -graphite-binder mixture with a solution of 1 Formal lithium perchlorate in propylene carbonate; dried by storing over molecular sieve (Linde Co. - Type 5A) for one week.

The conducting and supporting grid structure consisted of a  $1\frac{1}{2}'' \times 1\frac{5}{8}''$  sheet of 5-Ag-12.5-2/0 expanded silver mesh. Along one edge a 15 mil silver wire contact was spot-welded. Paste was applied to the grid, which was supported by a sheet of filter paper. After pasting, the electrode was placed between sheets of filter paper and pressed between heavy steel plates at prescribed compacting pressures. Finally, the electrodes were dried, under vacuum, in a dessicator containing drying agent.

Whenever possible, all procedures were carried out in a dry-box under argon or nitrogen atmospheres. However, because of practical limitations, it was necessary for certain operations, such as pressing, to be done in air.

#### 4.1.1.3 Electrode Testing

Before testing, electrodes were immersed overnight in dried propylene carbonate. The cathode was positioned between two lithium anodes in a

polypropylene container. Spacing between electrodes was approximately 1/4". A Luggin capillary opened to within one millimeter of the cathode surface and was connected with a reservoir containing a reference electrode. This technique reduced to a minimum the IR component of the observed potential.

The electrolyte used in the study was 1 Formal lithium perchlorate in propylene carbonate (dried).

Discharge was conducted at 50 ma ( $1.8 \text{ ma/cm}^2$ ) using a constant current D.C. power supply. Cathode potentials were taken against an  $\text{Li/Li}^+$  or  $\text{Ag/AgCl}$  reference electrode in the same electrolyte. A high impedance voltmeter, such as a Keithley Model 610 Electrometer, or a Hewlett Packard V.T.V.M. Model 412A, was used to measure potential. Tests were made in argon atmosphere. Discharge was terminated when the potential of the cathode was -3.0 volts vs.  $\text{Ag/AgCl}$  or 0.0 volts vs.  $\text{Li/Li}^+$ . (Percent theoretical  $\text{CuF}_2$  capacity discharge was taken as criterion of performance.)

#### 4.1.1.4 Results of Statistical Analysis

A typical discharge characteristic for a pasted  $\text{CuF}_2$  cathode is shown in Figure 12. The designation "Percent discharged" indicates the percent of total theoretical electrode capacity discharged.

As indicated above, a  $2^4$  factorial design was used to evaluate electrode fabrication parameters. This involved sixteen separate treatment combinations. The treatment combination is assigned a code letter as follows:

- 1- Refers to all variables in low value.
- a- Refers to variable  $\text{CuF}_2$  mesh size at high value (-325), all others low.
- b- Refers to graphite content at high value (10%), all others low.
- c- Refers to binder content at high value (2%), all others low.
- d- Refers to compacting pressure at high value ( $1000 \text{ lbs/cm}^2$ ), all others low.

The standard order of experiments is then seen to be: 1, a, b, ab, c, ac, bc, abc, d, ad, bd, abd, cd, acd, bcd, and abcd. This completely describes all possible treatment combinations. Results are shown in Table 13. The effects were evaluated as follows using the treatment of Yates (10):

The treatment combination is shown in the first column in standard order, and the coincident effect noted in column two. In the third column the effects, reduced by 12, are listed. This was done to simplify subsequent mathematical

operations. Columns 1, 2, 3 and 4 were derived from the third column by summing the eight pairs of results and then differencing. For example, the first figure in column 1 is obtained by adding 3.0 and 5.1 = 8.1 and the ninth figure is obtained by subtracting 3 from 5.1 to give 2.1. This is repeated for successive columns until column 4 is complete. Column 4 is then eight times the effect and this can be obtained by dividing the figures in column 4 by eight. The mean square is obtained by squaring the figures in column 4 and dividing by 16.

It is convenient to present the statistical analysis as shown in the analyses of variance Table 14. Since only two replicates were taken it was considered insufficient to use these as estimates of error. In this case, the higher order interactions can be used since these are generally small with respect to main and 2nd order effects. In Table 14 the error variance and significance level can be deduced as follows:

Sum of squares of 3rd and fourth order interactions	=	3.75
Degrees of freedom	=	5
Error mean square	=	$\frac{3.75}{5} = 0.75$

By applying an "F" test it can be shown that, for one and five degrees of freedom; the 5% value is 6.61. A mean square based on one degree of freedom is thus significant at the 5% level if it exceeds  $0.75 \times 6.61 = 4.95$ . This shows that the significant effects in Table 13 are a, b, c, d, ab, ac, and ad.

## DISCUSSION

Analyses has shown the following effects on percent utilization of  $\text{CuF}_2$  as a result of the various treatments:

- |   |                         |
|---|-------------------------|
| (a) Increase in $\text{CuF}_2$ mesh size<br>from -325 to -170 + 325 mesh    | Increase in utilization |
| (b) Increase in graphite content<br>from 5% to 10%                          | Increase in utilization |
| (c) Increase in binder content from<br>1% to 2%                             | Decrease in utilization |
| (d) Increase in compacting pressure<br>from 500 to 1000 lbs/cm <sup>2</sup> | Increase in utilization |



(e) Graphite -  $\text{CuF}_2$  interaction

Increase in utilization as result of increase in graphite content is greater with coarse as compared to fine particle  $\text{CuF}_2$ .

(f) Binder- $\text{CuF}_2$  interaction

Increase in binder content effects a greater reduction in utilization with fine as compared to coarse particle  $\text{CuF}_2$ .

(g) Compacting pressure  
 $\text{CuF}_2$  interaction

Increase in compacting pressure effects a greater utilization of  $\text{CuF}_2$  with fine rather than coarse particle powder.

Observation of physical characteristics of pasted cathodes revealed that they were generally fragile, and material could be easily dislodged from the grid unless gently handled. When immersed in electrolyte there was slight shedding of material, especially along the edges of the electrode. In this study maximum shedding was about 10%. After discharge, the active material was found to be soft and poorly adherent to the grid.

It was also observed that the electrolyte acquired a green color after the cathodes had been immersed for a short time. This appeared to be caused by dissolved  $\text{CuF}_2$ . During the latter part of the discharge, after the cathode had polarized more than a volt negative to  $\text{Ag}/\text{AgCl}$ , there was continuous gassing on the electrode until end of discharge.

## CONCLUSIONS

The most favorable combination of factors for best performance of pasted  $\text{CuF}_2$  cathodes, as evaluated in this test, appears to be as follows:

Use of coarse particle (-170 + 325 mesh)  $\text{CuF}_2$  powder, 10% graphite, 1% binder, and a compacting pressure of 1000 lb/cm<sup>2</sup>. The effect of  $\text{CuF}_2$  particle size variation observed in this study appears to contradict the hypothesis that better performance should be obtained with fine rather than coarse particle active material. The reason for this behavior is not immediately evident.

Extended evaluation of the factors found to be most significant in the factorial experiment was carried out. The experimental treatment was as follows:

	<u>Polystyrene Binder</u>	<u>Factors Graphite</u>	<u>CuF<sub>2</sub> mesh size</u>	<u>Compacting Pressure</u>
	1%	5%	-170 + 325	1000 and 2000 lb/cm <sup>2</sup>
Levels	1%	10%	"	" " "
	1%	15%	"	" " "
	1%	20%	"	" " "

Experiments were carried out in duplicate. Electrode fabrication technique and testing procedure were as previously described. Results of this experiment are shown in Table 15.

## DISCUSSION AND CONCLUSION

The results of this test are inconclusive because of the extreme shedding or blistering of the active material. Even in those electrodes where shedding was slight the extreme blistering caused the active material to become detached from the grid and thereby rendered ineffective. It was observed that a greater amount of shedding occurred in electrodes as the graphite content was increased. It appears that one percent binder is not sufficient to produce a structurally stable electrode when the graphite content is greater than five percent.

### 4.1.2 Hot Pressed CuF<sub>2</sub> Electrodes

An excellent method of making an electrode from powdered constituents is by hot pressing the active material in the presence of a thermoplastic binder. At elevated temperatures a certain amount of plastic flow is imparted to the mix which leads to extremely even pressure distribution in addition to the binding properties of the plastic. The thermoplastic binder chosen for the initial experiments was polyethylene powder. The electrodes were prepared as follows.

Cupric fluoride powder was sieved under a dry nitrogen atmosphere and mixed in the desired proportion with Southwestern 1651 micronized graphite. The powders were tumbled for 16 hours to achieve complete dispersion. The desired amount of -100 mesh polyethylene powder was added and the mix tumbled for a further 16 hours. Electrodes were die pressed at 90°C between sheets of vegetable paper for several minutes. This produced a fairly strong, uniform electrode.

#### 4.1.2.1 Factorial Statistical Analysis of Preparative Parameters

In order to determine which of the constituents was important in influencing the discharge characteristics a factorial statistical analysis was constructed to investigate the following factors each at two levels.

<u>Factor</u>	<u>Level (1)</u>	<u>Level (2)</u>
Amount of graphite	5%	10%
Amount of polyethylene	3%	5%
Compacting pressure	1000 lbs/cm <sup>2</sup>	2000 lbs/cm <sup>2</sup>
Pressing time	2 min.	3 min.

Electrodes of 1 1/2 in. x 1 5/8 in. were prepared in duplicate as described above from -170 mesh CuF<sub>2</sub> using a 5 Cu 14 2/0 expanded copper screen as the current collector. The electrodes contained approximately 1.8 gm of active material. Discharges were carried out in 1 Formal LiClO<sub>4</sub> in propylene carbonate at a current of 50 ma after an activated stand of 16 hours. The utilization of CuF<sub>2</sub> was used as the criterion of performance. The results were analyzed using Yates method and are shown in Table 16.

### DISCUSSION OF RESULTS

None of the effects observed exceeded the value required at the 5% significance level in this analysis. Therefore, none of the fabrication parameters tested could be considered to exert a significant effect on electrode performance. However, any significance that might have been obtained was probably obscured, owing to the considerable shedding of the electrodes during discharge. A true evaluation of the effect of fabrication parameters requires that the electrode remain structurally sound throughout the discharge.

Those factors that had the greatest effects, although not actually significant on the basis of the factorial analysis, were considered sufficiently important to justify further study. These will be considered next.

#### 4.1.2.2 Effect of Compacting Pressure on Performance

It had been observed during the statistical analysis that considerable shedding occurred during discharge of the electrodes. No shedding was observed during the open circuit period which suggests that changes in the volume of the electrode during discharge is responsible. It was considered that increasing the compaction of the electrode would alleviate this problem.

Hot pressed CuF<sub>2</sub> electrodes were prepared from a mix containing 85%, -170 mesh CuF<sub>2</sub>, 10% Southwestern 1651 graphite and 5%, -100 mesh polyethylene. The electrodes were pressed at 90°C for 3 min. at pressures ranging from 1000 lbs/cm<sup>2</sup> to 6500 lbs./cm<sup>2</sup>. These were discharged in 1 Formal LiClO<sub>4</sub> in propylene carbonate at a current of 50 ma (1.8 ma/cm<sup>2</sup>). The electrode potential was measured with respect to a lithium reference electrode in the same electrolyte. The results are shown in Figure 13. Increasing the pressure causes

an increase in performance up to 3000-4000 lb/cm<sup>2</sup>. Above this the performance decreases again. Figure 14 shows a plot of percent utilization versus pressure.

The problem of shedding was largely overcome at the higher pressures; the electrodes however had a wrinkled appearance after discharge.

#### 4.1.2.3 Effect of Graphite on Performance of Hot Pressed Electrodes

The most significant effect observed during the statistical analysis was the increase in utilization on increasing the amount of graphite in the electrode. An experiment was carried out to determine the optimum concentration. Hot pressed electrodes were prepared from a mixture of -170 mesh CuF<sub>2</sub>, Southwestern 1651 graphite and polyethylene powder pressed at 4000 lbs/cm<sup>2</sup> for 3 min. at 90°C. The amount of graphite varied from 10% to 22% and the amount of binder was held constant at 5%. The electrodes were discharged at 50 ma (1.8 ma/cm<sup>2</sup>) in 1 Formal LiClO<sub>4</sub> in propylene carbonate as described above. The results are shown in Figure 15.

The results are rather difficult to interpret because at the higher graphite levels progressively more shedding of the electrode was in evidence. Since the density of graphite is low the effectiveness of the binder is lessened as the amount of graphite is increased. There thus appears to be an interaction between the graphite and binder which would be best examined by statistical analysis. It can be concluded however that increasing the amount of graphite above 10% does not improve the electrode performance. We would expect therefore to obtain the highest energy density from electrodes containing only a small amount of graphite.

#### 4.1.2.4 Effect of Amount of Binder on Hot Pressed Electrodes

Although the mechanical strength of the electrodes was adequate if they were handled gently there was danger of breakage if they were not treated with care. The effect of the amount of binder on the performance was investigated to determine whether the electrodes could be made tougher without impairing the performance. Electrodes were prepared from the following mixes.

i	87.5% CuF <sub>2</sub>	10% graphite	2.5 % polyethylene
ii	85% CuF <sub>2</sub>	10% graphite	5% polyethylene
iii	83.6% CuF <sub>2</sub>	10% graphite	6.4% polyethylene
iv	81.7% CuF <sub>2</sub>	10% graphite	8.3% polyethylene

The electrodes were hot pressed at 4000 lbs/cm<sup>2</sup> for 3 minutes at 90°C and discharged as above. The results are shown in Figure 16.

Increasing the amount of binder resulted in a more robust structure which could be handled without damage; however, the performance on discharge was consider-

ably reduced. When the electrodes were removed from the cell after discharge those with the increased amount of binder appeared wet-proof which possibly indicates considerable masking of the surface by the polyethylene.

#### 4.1.2.5 Effect of Particle Size of $\text{CuF}_2$ on Performance of Hot Pressed Cathodes

The particle size of the  $\text{CuF}_2$  is an important parameter since it influences the surface area, thus the true current density, the porosity and pore size distribution of the electrode. The factorial statistical analysis carried out on the pasted electrodes had indicated that better performance was obtained from the larger particles and so it was decided to investigate whether the same effect was evident in the hot pressed type.

Electrodes were prepared from a mix of 85%  $\text{CuF}_2$ , 10% graphite and 5% polyethylene by pressing at 2000 lbs/cm<sup>2</sup> for 3 minutes at 90°C. Three particle size ranges of  $\text{CuF}_2$  were investigated.

- (i) -80 to +170 mesh
- (ii) -170 to +325 mesh
- (iii) -325 mesh

The electrodes were discharged at 1.8 ma/cm<sup>2</sup> as described before. The results are shown in Figure 17. The electrodes prepared from coarse particle  $\text{CuF}_2$  performed better than those with fine -325 mesh particle material. Electrode potentials were somewhat better with -80 to +170 mesh material than with -170 to +325 powder, but utilization was about the same for both materials.

#### 4.1.2.6 Discharge of Hot Pressed Cupric Fluoride Electrodes in 1M $\text{LiClO}_4$ Dimethyl Sulphoxide

Corrosion and solubility screening tests had shown that lithium and  $\text{CuF}_2$  were only slightly attacked by DMSO. In addition the conductance of DMSO solutions is higher than propylene carbonate solutions of the same ionic strength.

A group of electrodes was prepared from a mix containing 85%  $\text{CuF}_2$ , 10% graphite and 5% polyethylene. They were hot pressed at 90°C for 3 minutes at 2000 lbs/cm<sup>2</sup> and discharged in 1 Formal  $\text{LiClO}_4$  in DMSO at 1.8 ma/cm<sup>2</sup>. A typical result is shown in Figure 18.

The utilization was average but the polarization was much greater than in the propylene carbonate solution. During the second step in the discharge curve considerable gassing occurred at the cathode accompanied by an unpleasant sulphurous odor. This was probably due to reduction of the solvent. On the basis of this experiment DMSO does not appear to be a suitable solvent for electrolytes for  $\text{CuF}_2$  electrodes.

#### 4.1.2.7 Substitution of Lampblack for Graphite

Lampblack has the ability to absorb fairly large quantities of electrolyte. This is potentially a very desirable feature since a high energy density battery would have very little free electrolyte. Thus, electrolyte could be supplied to the reaction site, perhaps removing some of the more transparent problems associated with porous electrodes.

We prepared electrodes containing 5% graphite and 5% lampblack, and these were compared to the standard 10% graphite electrodes. The strength of the lampblack containing electrodes was lower than the standard electrode and there was a slight tendency to shed during the open circuit stand. The electrodes were discharged at  $1.8 \text{ ma/cm}^2$  in 1 Formal  $\text{LiClO}_4$  in propylene carbonate.

Results of typical electrodes are shown in Figure 19.

The performance of the lampblack containing electrode is surprisingly poor. This is probably because of the shedding which allowed approximately half of the active material to fall off. This is in contrast to the 10% graphite electrode which did not shed during the charge.

#### 4.1.3 Pressed Cylindrical Electrodes

One of the problems in the construction of a high energy density battery is the relatively high ratio of grid weight to active material weight. This is especially true when the active materials are light such as lithium and cupric fluoride. For example, if we consider a typical hot pressed electrode as described previously the gravimetric composition might typically be:

Wt of grid (5 Cu 14 2/0) 1 1/2 in. x 1 5/8 in.	= 0.52g
Wt of $\text{CuF}_2$	= 1.70g
Wt of graphite	= 0.20g
Wt of binder	= 0.10g

Thus 32.6% of the electrode is inert material which seriously reduces the energy density. If an electrode could be fabricated without a grid or with at most a fine contact wire then the proportion of grid weight would be very much reduced. One of the problems associated with electrodes having contact only by a wire is the long resistive path from the reaction site to the current collector which usually leads to appreciable I.R. losses. The most favorable geometry is thus a cylindrical electrode with a contact wire down the center. A number of cylindrical electrodes were prepared by die pressing the standard hot pressed electrode mix at  $9000 \text{ lbs/cm}^2$  into cylinders 0.78 cm diam. x 1.4 cm long. Electrical contact was made via a 0.028 in Cu wire down the center of the electrode. Typical material weights for this type of construction were:

Wt of contact wire = 0.07g

Wt of  $\text{CuF}_2$  = 1.70g

Wt of graphite = 0.20g

Wt of polyethylene = 0.10g

The amount of inert material was thus reduced to 17.9% of the electrode weight. A further reduction in the weight of the inert material could be made by eliminating the binder which does not appear to be necessary in this type of construction. Figure 20 shows a typical discharge curve for this type of electrode taken at 2.0  $\text{ma/cm}^2$  in 1 Formal  $\text{LiClO}_4$  in propylene carbonate. The utilization is lower than obtained from an optimized hot pressed electrode; the capacity per gram of electrode weight is however higher due to the reduction in grid weight. With optimization of the preparative parameters this type of electrode may possibly give better performance than the hot pressed type.

#### 4.1.4 Electroformed $\text{CuF}_2$ Cathodes

In order to realize maximum energy density from electrodes it will be necessary to eliminate, or reduce considerably the amount of, electrochemically inactive additives such as graphite and binder. One method whereby this may be accomplished is by electroforming  $\text{CuF}_2$  on a porous sintered copper matrix. This type of electrode will require no binder or graphite, because the sintered copper matrix is both structurally strong and a good electrical conductor.

In a study by H. Schmidt (11), anhydrous halides of several metals were produced when using these metals as anodes in an electrolyte containing a halide of a more noble metal. Acetonitrile was used as a solvent.

Although the primary objective of this study was to produce soluble anhydrous halides, as compared to the insoluble halide required with  $\text{CuF}_2$  cathodes, it did show that halides could be electroformed with nearly 100% current efficiency. No reference was made to work with fluorides.

The first requirement in this work is a non-aqueous, fluoride containing electrolyte in which  $\text{CuF}_2$  can be electroformed, and in which it will be insoluble. The solubilities of  $\text{KF}$ ,  $\text{LiF}$ , and  $\text{HgF}_2$  in acetonitrile, propylene carbonate, nitromethane and glacial acetic acid were studied. Only glacial acetic acid was found to be capable of dissolving fluorides to an appreciable extent. An electrolyte was made composed of half formal each lithium perchlorate and lithium fluoride in glacial acetic acid.

Two sheet metal copper electrodes were immersed in the electrolyte and a d. c. current passed through the cell. The anode dissolved to produce a dark blue reaction product which was soluble in the electrolyte. No attempt was made to analyze the product since the required insolubility of the anode produce was not obtained with this system.

Further efforts are in progress in the study of electroforming  $\text{CuF}_2$ . At the present time they are concerned primarily with further literature search of methods of electroforming halides in non-aqueous systems.

#### 4.2 Cobalt Trifluoride Cathodes

Cobalt trifluoride cathodes were prepared by hot pressing a mix of the following composition:

85%	-170 mesh $\text{CoF}_3$
10%	Southwestern 1651 graphite
5%	-100 mesh polyethylene

The electrodes were pressed at  $90^\circ\text{C}$  for 3 minutes at  $2000 \text{ lbs/cm}^2$ . These were then discharged in 1 Formal  $\text{LiClO}_4$  in propylene carbonate at  $1.8 \text{ ma/cm}^2$ . The discharge curve of a typical electrode is shown in Figure 21.

The performance is considerably poorer than a corresponding  $\text{CuF}_2$  electrode, the polarization being much greater and the utilization poor. Some promise is shown, however, which possibly justifies further work.

#### 4.3 Chromium Trifluoride Electrodes

These electrodes were prepared and discharged identically to the  $\text{CoF}_3$  electrodes described above. The performance is shown in Figure 21. Extremely high polarization was observed and the capacity was very poor.

### 5. Thermodynamic Studies - Li - $\text{CuF}_2$ Cell

Cell voltage data obtained over the range  $15^\circ\text{C}$  -  $50^\circ\text{C}$  were used to calculate values of free energy, enthalpy and entropy for the reaction  $2 \text{ Li} + \text{CuF}_2 \rightarrow 2 \text{ LiF} + \text{Cu}$ .

#### 5.1 Experimental Procedure

An "H" shaped glass cell was used, containing in each arm one of the electrodes, and filled throughout with electrolyte. The bridge between the arms was a 20 in. long capillary tube with a one millimeter bore. Where this tube joined the cathode well, a tight fitting filter paper plug, 1 in. long, was inserted into the bore. This technique was used to reduce, to a minimum, the amount of dissolved  $\text{CuF}_2$  diffusing to the anode.

The electrodes were made using platinum screen to support the active materials. A platinum contact wire was welded to each screen. The anode was made by pressing lithium ribbon (Foote Mineral Co.) into the screen at a pressure sufficient to give good adhesion. The cathode was prepared using the technique already described. (Section 4.1)



The opening in each arm of the cell was sealed with a Teflon stopper in which holes were drilled to accommodate gas fittings and the electrode contact wires.

The electrolyte was 1 Normal lithium perchlorate (anhydrous) in twice-distilled propylene carbonate. Dry argon gas was bubbled through the electrolyte in each arm of the cell to prevent air and moisture from entering the system.

The cell was partially immersed in a thermostatically controlled water bath, where temperatures were maintained within  $\pm 0.1^\circ\text{C}$  over the range  $15^\circ\text{C}$  to  $50^\circ\text{C}$ .

Immediately after activation with electrolyte, cell voltage was unstable. After standing at  $25^\circ\text{C}$  for about sixteen hours reproducible cell voltages could be obtained. The temperature was then varied, and a period of about one hour was allowed for equilibration at each temperature before voltages were measured. A Rubicon Potentiometer (Model 2780 S) was used to measure the cell potential.

## 5.2 Results and Discussion

Two voltage-temperature runs were made on two successive days. Cell voltage decreased slowly with time, but this did not appreciably affect the temperature coefficient of voltage  $\frac{\partial E}{\partial T}$ , which can be seen from Table 17 and Figure 22.

These values agree to within one-half percent.

The Gibbs-Helmholtz equation,  $\Delta H = -nF \left[ E - T \left( \frac{\partial E}{\partial T} \right)_p \right]$  was used to

to obtain values of  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  for the reaction  $2 \text{Li} + \text{CuF}_2 \rightarrow 2 \text{LiF} + \text{Cu}$ . The calculated values, obtained using cell voltage data, are shown in Table 17. The values of  $\Delta G$  at  $25^\circ\text{C}$  agree on the average, to within one-half percent, with  $\Delta G$  at  $25^\circ\text{C}$  calculated from literature values of the thermodynamic properties of the reactants involved,  $-163 \text{ kcal}$  (12, 13).

The values of  $\Delta H$  at  $25^\circ\text{C}$  for the reaction, calculated from literature values of heats of formation of the reactants involved, was greater, by  $-23$  to  $-25 \text{ kcal}$ , than values obtained from this study. It should be noted that all literature values of the properties are obtained from the elements or compounds in the crystalline state. The values calculated, using data from this test, are based on reactant in solution, with heats of ionization and solution possibly involved. This may account for the differences observed. The value of  $\Delta S$  at  $25^\circ\text{C}$  for the reaction was calculated from cell voltage data using the formula  $\Delta S = nF \frac{\partial E}{\partial T}$ . The

values obtained (Table 17) indicate a positive entropy for the reaction. This means an absorption of heat during the process.

The values of  $\Delta G$  at various temperatures are shown in Figure 23, which reveals a linear relationship. The increase in  $\Delta G$  with increase in temperature is about  $+0.075 \text{ kcal}/^\circ\text{C}$ .

## CONCLUSION

The value of  $\Delta G$  at 25°C obtained in this study agrees to within 1/2% with literature values for the reaction  $2\text{Li} + \text{CuF}_2 \rightarrow 2\text{LiF} + \text{Cu}$ . This appears to indicate the stated reactions are reversible.

### 6. Effect of Current Density on Performance

A number of hot pressed  $\text{CuF}_2$  electrodes were prepared from the following mix.

85% Ozark-Mahoning  $\text{CuF}_2$  (-170 - 325 mesh)  
10% Southwestern 1651 micronized graphite  
5% Polyethylene powder (-100 mesh)

The electrodes were pressed at 90°C for 3 minutes at a pressure of 3000 lbs/cm<sup>2</sup>.

The discharge was carried out in a specially designed cell shown in Figure 24. The electrodes were given a 16 hour stand in 1 Normal  $\text{LiClO}_4$  in propylene carbonate and then mounted in the cell which was maintained at 25°C. One Normal  $\text{LiClO}_4$  solution was then added and the atmosphere above the electrolyte purged with dry nitrogen or argon. The electrode potential was measured with reference to a lithium electrode in the same electrolyte using a Keithley electrometer Model 610 in conjunction with a Varian Associates Model 9-14 graphic recorder. Chronopotentiograms were obtained over a wide range of current densities. The results are shown in Figure 25.

At the lower current densities the discharge curve exhibits two well defined plateaus of roughly equal capacity. As the current density is increased the second plateau diminishes rapidly until at 3.0 ma/cm<sup>2</sup> it has disappeared. The first plateau is only affected slightly by increasing the current density and over 40% of the capacity is obtained at 5 ma/cm<sup>2</sup>. An experiment was conducted to determine the effect of current density on the polarization of the  $\text{CuF}_2$  cathode during the first plateau. A cupric fluoride electrode of the type used previously was polarized at successively increasing current densities. Since the potential was continuously changing with time we decided to record the potential 100 milliseconds after closing the circuit. The potential transient was recorded on a Tektronik oscilloscope Type 535 and photographed for further analysis. This allowed the elimination of the IR drop from the polarization. After the transient had been recorded the circuit was opened and the electrode potential allowed to return to its original open circuit value when the experiment was repeated at a higher current density. The results are shown in Figure 26 where potential is plotted against current density.

A straight line plot is obtained which is typical of a reaction in which the overpotential is low. In the electrokinetic equation

$$i = i_0 \left[ \exp \frac{a n F E}{RT} - \exp \frac{(1-a) n F E}{RT} \right]$$

where  $i$  = current density  
 $i_0$  = exchange current density  
 $a$  = transfer coefficient  
 $E$  = polarization

and the other symbols have their usual meaning. If the polarization is low then the exponential terms will be small and can be expanded to give

$$i = i_0 \left[ 1 + \frac{anFE}{RT} - 1 + \frac{(1-a) nFE}{RT} \right]$$

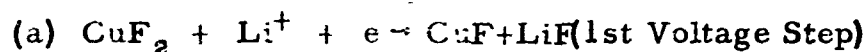
$$i = i_0 \left[ \frac{anFE}{RT} + \frac{(1-a) nFE}{RT} \right]$$

$$i = i_0 \left[ \frac{nFE}{RT} \right]$$

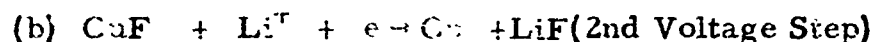
and a plot of current density against polarization gives a straight line.

#### 6.1 X-Ray Diffraction Studies

An experiment was designed to determine the reaction products at various stages of discharge of the  $\text{CuF}_2$  cathode. This was done to determine if the discharge proceeds in two steps, thus accounting for the two sharply defined voltage steps in the discharge curve. If it is assumed that the following reactions occur:



and



then an analyses of reaction products at various stages of discharge should reveal the presence of  $\text{CuF}$  and  $\text{LiF}$  before the break in the discharge curve, and  $\text{CuF}$  and  $\text{Cu}$  after the break.

A series of discharges was conducted with electrodes, one inch square, of the hot pressed type previously described.

The electrolyte used in the experiment was 1 Formal lithium perchlorate in propylene carbonate. All discharges were at a current density of  $0.5 \text{ ma/cm}^2$ . Voltages of the test electrode were measured against an  $\text{Li/Li}^+$  reference electrode in the same electrolyte. A Keithley Electrometer was used to measure potentials, and a d. c. constant current power supply used to discharge the cell.

Each electrode was discharged to a prescribed level, after which the electrode

was analyzed, by x-ray diffraction, to determine the composition of reaction products. The points at which the various electrodes were removed for analysis are shown by the letters A through E in Figure 27. The compounds present in the electrode immediately after fabrication were determined with an undischarged electrode.

The results of this study are shown in Figure 26. Analyses revealed that copper was produced throughout the discharge, in gradually increasing quantities, as was lithium fluoride. No cuprous fluoride was detected at any stage of discharge. The relative amounts of products formed during the discharge are indicated by the symbol  $>$  and  $<$  to indicate respectively, quantities greater than, or less than, another quantity. For example, at stage B, the amount of copper is indicated as  $\text{Cu} > \text{A}$ , indicating that the amount of copper detected is greater than that found at stage A.

The fact that no cuprous fluoride ( $\text{CuF}$ ) was detected at any stage of discharge appears to indicate that  $\text{CuF}$  is not a stable intermediate in the reaction. However, if it assumed that  $\text{CuF}$  is formed, but is then rapidly reduced to  $\text{Cu}$ , this would be consistent with the analysis. If the reaction is actually a two electron change process, i.e.,  $\text{CuF}_2 + 2 \text{Li}^+ + 2 \text{e}^- \rightarrow \text{Cu} + 2 \text{LiF}$ , the observed break in the discharge curve must be due to other factors. Possibly a diffusion process may be involved, coupled with changes in resistive polarization.

## 7. Lithium Electrode Studies

### 7.1 Pressed Foil Electrodes

One of the simplest techniques of preparing lithium electrodes is by pressing lithium foil into a retaining grid. It was decided to investigate this method as a possible fabrication technique.

The electrodes were prepared as follows. Lithium ribbon 1/2 in. wide by 1/16 in. thick (Foote Mineral Co.) was cut into 2 in. long pieces and pressed at 12,000 lbs. between stainless steel platens greased with petrolatum (1). This deformed the lithium into a sheet approximately 1.5 in. wide and 0.010 in. thick. The foil was cut to the desired size of 1.5 in. x 1.5 in. and pressed at 12,000 lbs. into a 2/0 expanded copper grid. Since the lithium ribbon and the platens were well greased oxidation was only slight. The electrodes were then transferred to a glove box filled with dry argon and cleaned as follows.

- (i) Degrease in n-hexane
- (ii) Etch in absolute methanol until oxide free
- (iii) Etch in 50/50 methanol propylene carbonate mixture
- (iv) Wash three times in twice distilled propylene carbonate
- (b) Store in screw top jars in twice distilled propylene carbonate

In this way a clean shiny electrode is obtained which can be stored for long periods without dulling. The electrodes were discharged against lithium counter electrodes in 1 Formal  $\text{LiClO}_4$  in propylene carbonate at  $1.8 \text{ ma/cm}^2$ . A typical discharge curve is shown in Figure 28. Seventy to seventy-five percent of the theoretical capacity can be realized from this type of electrode. The main cause of premature failure appears to be uneven dissolution of the lithium thus causing perforation and detachment of pieces of active material.

## REFERENCES

- (1) Fleischer, A., Background Material for the Study of the National Space Power Program, AD 452617, 1964, Volume 1, Electrochemical Papers.
- (2) Latimer, W. M., "Oxidation Potentials", Prentice-Hall, Inc. 1953.
- (3) T. Shedlovsky, J. Am. Chem. Soc. 54, 1405 (1932).
- (4) W. S. Harris, Electrochemical Studies in Cyclic Esters, UCRL 8381 Contract No. W-7405 - eng. - 48.
- (5) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Academic Press Incorporated 1959.
- (6) B. F. Wishaw and R. H. Stokes, J. Am. Chem. Soc. 76, 2065 (1954).
- (7) J. S. Dunnett and R. P. H. Gasser, Trans. Farad. Soc. 61, 922 (1965).
- (8) C. B. Monk, "Electrolytic Dissociation", Academic Press 1961.
- (9) R. M. Fuoss and F. Accascina, "Electrolytic Conductance", Interscience Publishers Inc. 1959.
- (10) O. W. Davies, "The Design and Analysis of Industrial Experiments", Hafner Publishing Company, 1956.
- (11) H. Schmidt, Electrolysis in Acetonitrile, z. anorg. allg. Chemie, 271:305-320, 1953.
- (12) W. M. Latimer, Oxidation Potential, Prentice-Hall, Inc., 1953.
- (13) Handbook of Chemistry and Physics, 45th Edition, 1964-1965.

TABLE 1

Battery	Theoretical Energy Density (w-hr/lb)	Practical Energy Density (w-hr/lb)
Nickel/Cadmium	107	12-15
Silver/Cadmium	120	20
Silver/Zinc	208	40

TABLE 2

Battery	Energy 1963	Density 1968	Forecast (w-hr/lb) 1975
Ni/Cd	12	13.5	15
Ag/Cd	20	22	24
Ag/Zn	40	40	40
Leclanche	25	30	40
Zn/Hg O	45	5	60
Mg/m - C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub>	70	100	130
Mg/Ag Cl	22	28	35
Mg/Cu Cl	15	20	25



TABLE 3

Anode	Equivalent Weight	Equivalents/ Mole	Amp-hr/g ( $M \rightarrow M^{n+} + ne$ )	$\Delta F^\circ$ ( $MF_n$ )	$E^\circ$ ( $M \rightarrow M^{n+} + ne$ )
Li	6.9	1	3.88	-139.6	-3.045
Na	22.99	1	1.17	- 56.7	-2.714
K	39.10	1	0.68	-127.42	-2.925
Rb	85.48	1	0.31	-124.3	-2.925
Co	132.91	1	0.20	-119.5	-----
Mg	12.16	2	2.20	-250.8	-2.37
Al	9.00	3	2.98	-294.0	-1.66
Ca	20.04	2	1.31	-277.7	-2.87
Zn	32.69	2	0.82	-----	-0.763

TABLE 4

Compound	Equivalent Weight	Equivalents/ Mole	Amp-hr/g ( $MX_n + ne \rightarrow M + nX^-$ )	$\Delta F^\circ$ (Kcal/mole)
CuF <sub>2</sub>	50.75	2	0.528	-116
CoF <sub>3</sub>	38.64	3	0.695	-250
PbF <sub>2</sub>	122.60	2	0.219	-148.1
NiF <sub>2</sub>	48.34	2	0.555	-148.8
AgF	126.88	1	0.212	- 44.2
CrF <sub>3</sub>	36.40	3	0.737	-248.3

TABLE 5

<u>Couple</u>	<u>Cell Volts</u>	<u>W-hrs/lb</u>
Li/CuF <sub>2</sub>	3.54	746
Li/CoF <sub>3</sub>	3.63	970
Li/PbF <sub>2</sub>	2.84	266
Li/NiF <sub>2</sub>	2.82	620
Li/AgF	4.12	375
Li/CrF <sub>3</sub>	2.46	692
Li/TiF <sub>4</sub>	2.30	516

TABLE 6

Solvent	M Pt °C	B Pt °C	Density g/cc	Viscosity cp (25°C)	Vapour Pressure mm Hg (25°C)	Di electric Constant
Acetonitrile	-42	82.0	0.7828	0.36		38.8
Acetone	-95	56.5	0.792	0.302	229.2	20.7
Di methyl formamide	-61	153	0.9445	0.633	3.7	36.71
Di methyl sulphoxide	6	189	1.099	1.93	0.60	48.0
Ethyl Acetate	-83.6	77.15	0.901	0.409	72.80	6.4
Di methyl sulphate	-31.8	188	1.3322	2.73 (0°C)	40	55.0
Nitromethane	-29	101	1.130	0.619	< 1.0	39.4
Nitroethane	-50	114.8	1.052			30.6
Propylene Carbonate	-49.2	241.7	1.198	2.201		64.4

TABLE 7

Equivalent Conductance of  $\text{LiClO}_4$  in Propylene Carbonate

Concentration (F)	$\sqrt{\text{Concentration}}$	Equivalent Conductance $\Lambda$
0.002	0.0442	24.80
0.004	0.0632	24.08
0.006	0.0774	23.61
0.008	0.0894	23.20
0.010	0.1000	22.85
0.020	0.1415	21.60
0.028	0.1637	20.91
0.050	0.2237	19.62
0.100	0.316	18.30
0.500	0.707	11.24
1.000	1.000	7.26
1.500	1.225	3.92

**TABLE 8****Viscosity and Density of LiClO<sub>4</sub> in Propylene Carbonate**

<b>Concentration (F)</b>	<b>Density (g/ml)</b>	<b>Viscosity (cp)</b>
0.002	1.06397	2.2033
0.004	1.06437	2.2035
0.006	1.06442	2.2061
0.008	1.06462	2.2063
0.010	1.06481	2.1929
0.020	1.06541	2.2231
0.028	1.06499	2.2224
0.050	1.06551	2.2977
0.200	1.06879	2.6354
0.300	1.07040	2.8635
0.400	1.07209	3.1479
0.500	1.07472	3.5247
0.600	1.07579	3.8595
0.800	1.07944	4.8512
1.000	1.08379	6.1875

TABLE 9

## Comparison of Observed and Calculated Conductances

Concentration	$C^{1/2}$	$\eta$ (cp)	$\eta^\circ/\eta$	$\Lambda_{obs}$	$\Lambda$ calculated					$\Lambda \eta$ calculated				
					$a^\circ$					$a^\circ$				
					$a^\circ=4$	$a^\circ=3$	$a^\circ=2.5$	$a^\circ=2$		$a^\circ=4$	$a^\circ=3$	$a^\circ=2.5$	$a^\circ=2.0$	
0.002	0.0442	2.2033	0.999	24.80	24.837	24.813	24.804	24.789		24.812	24.788	24.779	24.764	
0.004	0.0632	2.2035	0.999	24.08	24.231	24.089	24.165	24.141		24.207	24.065	24.140	24.117	
0.006	0.0774	2.2061	0.998	23.61	23.804	23.736	23.705	23.670		23.756	23.688	23.657	23.623	
0.008	0.0894	2.2063	0.998	23.20	23.452	23.457	23.415	23.279		23.405	23.410	23.368	23.232	
0.010	0.1000	2.1929	0.997	22.85	23.237	23.052	22.997	22.924		23.167	22.983	22.928	22.855	
0.020	0.1415	2.2231	0.992	21.60	22.060	21.879	21.784	21.677		21.883	21.704	21.609	21.503	
0.050	0.2237	2.2977	0.957	19.62	20.225	19.852	19.808	19.421		19.396	19.038	18.996	18.625	
0.100	0.3160	2.3750	0.927	18.30	18.549	17.947	17.609	17.213		17.194	16.636	16.323	15.956	
0.500	0.7070	3.5247	0.627	11.24	14.041	12.539	11.643	10.528		8.804	7.861	7.300	6.601	
1.000	1.0000	6.1875	0.356	7.26	12.067	10.079	10.428	7.411		4.296	3.588	3.712	2.638	

Solubility of Cathode Materials in  
Electrolyte after Four Days

Visual Comparison

Electrolyte	CuF <sub>2</sub>	CrF <sub>3</sub>	CoF <sub>3</sub>
1F KCNS in Acetonitrile	3	3	3
1.5F LiClO <sub>4</sub> in Acetonitrile	2	1	1
1F AlCl <sub>3</sub> in Acetonitrile	2	3	3
1.5F LiClO <sub>4</sub> in Nitromethane	2	3	2
1F AlCl <sub>3</sub> in Propylene Carbonate	3	3	2
1F LiCl in Propylene Carbonate	1	1	1
1F LiCl in DMF	2	--	--
0.26F LiClO <sub>4</sub> in DMF	1	1	1
1F LiClO <sub>4</sub> in DMSO	1	1	1

DMF = Di Methyl Formamide

3 = Highly colored solution

2 = Moderately colored solution

1 = Slightly colored solution

Table 10



TABLE 11

Variation of Potential of Lithium Electrode with Concentration

Solution 1 (Formal)	Solution 2 (Formal)	Potential (volts)
0.5	0.1	-0.0430
0.5	0.2	-0.0226
0.5	0.3	-0.0105
0.5	0.4	-0.00325
0.5	0.5	0.00
0.5	0.6	0.0080
0.5	0.8	0.02075
0.5	1.0	0.0250

TABLE 12

Solution 1 (Formal)	Solution 2 (Formal)	Ej (volts)	Corrected EMF (volts)
0.5	0.1	-0.007	-0.0360
0.5	0.2	-0.004	-0.0186
0.5	0.3	-0.002	-0.0085
0.5	0.4	-0.001	-0.00225
0.5	0.5	0.000	0.00
0.5	0.6	0.001	0.0070
0.5	0.8	0.003	0.01775
0.5	1.0	0.004	0.0210

TABLE 13

## Analysis of Results of Factorial Experiment

Effect - Percent Utilization of  $\text{CuF}_2$ 

Treatment Combination (a)	Percent Utilization (b)	Column (b) Reduced by 12	1	2	3	4	Effect	Mean Square
	Mean value							
1	15	3.0	8.1	41.35	73.75	186.5		
a	17.1	5.1	33.25	32.40	112.75	-21	-2.62	27.5
b	32.8	20.8	3.2	63.35	-19.25	110.8	13.9	767.2
ab	24.4	12.4	29.2	49.40	-1.75	-43.6	-5.45	118.8
c	14.6	2.6	15.75	-6.25	51.15	-22.9	-2.55	32.7
ac	12.6	0.6	47.6	-13.0	59.65	-14.2	-1.77	12.6
bc	32.1	20.1	10.8	2.85	-19.45	-3.2	-0.4	0.64
abc	21.1	9.1	38.6	-4.6	-24.15	3.6	0.45	0.81
d	17.3	5.3	2.1	25.15	-8.95	39.0	4.87	95
ad	22.4	10.4	-8.35	26.0	-13.95	17.5	2.18	19.1
bd	39.8	27.8	-2.0	31.85	-6.75	8.5	1.06	4.5
abd	31.8	19.8	-11.0	27.8	-7.45	-4.7	-0.59	1.38
cd	15.8	3.8	5.15	-10.45	0.85	-5.0	-0.63	1.5
acd	19.0	7.0	-8.0	-9.0	-4.05	-0.7	-0.08	0.03
bcd	35.2	23.2	3.2	-13.15	1.45	-4.9	-0.61	1.5
abcd	27.4	15.4	-7.8	-11.0	2.15	0.7	-0.08	0.03

TABLE 14

## Analysis of Variance

Source of Variance	Mean Square	Degrees of Freedom	Effect
a	27.5	1	-2.62
b	767.2	1	13.9
c	32.7	1	-2.55
d	95.0	1	4.87
ab	118.8	1	-5.45
ac	12.6	1	-1.77
ad	19.1	1	2.18
Higher Interaction		5	

**TABLE 15****Pasted  $\text{CuF}_2$  Cathodes****Extended Evaluation of Graphite and Compacting Pressure Levels**

Binder Level Throughout - 1%  
 $\text{CuF}_2$  Mesh Size - 170 + 325

Treatment Combination		Percent Utilization $\text{CuF}_2$	Remarks
Percent Graphite	Compacting Pressure #/cm <sup>2</sup>		
5	1000	50.6	Slight Shedding But Blistered
"	"	52.8	
"	2000	48.7	Slight Shedding But Blistered
"	"	47.2	
10	1000	24.8	25 - 30% Shedding and Blistered
"	"	24.8	
"	2000	37.2	25% - 30% Shedding and Blistered
"	"	32.6	
15	1000	38.8	25% Shedding and Blistered
"	"	31.0	
"	2000	---	Not Tested. More than 50% Shedding
"	"	---	
20	1000	31.2	Extreme Blistering 10% Shedding
"	"	38.7	
"	2000	29.3	Extreme Blistering 10% Shedding
"	"	33.7	

TABLE 16

## Statistical Analysis of Hot Pressed Electrodes

Treatment Combination	Efficiency	1	2	3	4	Effect	Mean Square
0	36.8	81.6	164.2	294.9	531.6		
a	44.8	82.6	130.7	236.7	90.6	11.3	512
b	42.8	56.7	122.8	19.3	32.2	4.025	62.7
ab	39.8	74.0	113.9	71.3	45.2	5.65	125
c	35.4	65.0	5.0	18.3	-42.4	-5.3	112.5
ac	21.3	57.8	14.3	13.9	70.6	9.5	310.0
bc	22.8	46.4	5.0	31.5	44.6	5.6	124
abc	51.2	67.5	66.3	13.7	80.4	10.00	405
d	29.6	8.0	1.0	-33.5	-58.2	-7.3	212
ad	35.4	-3.0	17.3	-8.9	52.0	6.5	169
bd	29.3	-14.1	-7.2	9.3	-4.4	-0.55	1.21
abd	28.5	28.4	21.1	61.3	-17.8	-2.22	19.8
cd	11.7	5.8	-11.0	28.3	24.6	3.10	37.9
acd	34.7	-0.8	42.5	53.5	52.0	6.5	169
b.c.d	12.1	23.0	-6.6	26.9	12.0	1.5	9.0
a.b.c.d.	55.4	43.3	20.3		-26.6	-3.32	44.2

Analysis of Variance

Sum of squares of 3 and 4 factor interactions	= 647.0
Degrees of freedom	= 5.0
Mean Square	= 129
Minimum mean square for significance at 5% level	= 854
Minimum mean square for significance at 10% level	= 520

TABLE 17

Thermodynamic Properties at Various Temperatures  
for the Li - CuF<sub>2</sub> Cell

Run # 1	Temperature °C	E Volts	$\frac{\partial E}{\partial T}$	$\Delta G$ Kcalories	$\Delta H$ Kcal.	$\Delta S$ Kcal/deg.
"	15	3.5473	+0.00162	-163.60	-142.08	+0.0747
"	20	3.5555	"	-163.98	-142.09	"
"	25	3.5635	"	-164.35	-142.08	"
"	30	3.5715	"	-164.72	-142.08	"
"	35	3.5795	"	-165.09	-142.08	"
"	40	3.5880	"	-165.48	-142.09	"
"	45	3.5960	"	-165.85	-142.09	"
"	50	3.6043	"	-166.23	-142.09	"
1 Run # 2	15	3.5082	+0.00161	-161.80	-140.41	+0.0742
"	20	3.5162	"	-162.17	-140.41	"
"	25	3.5242	"	-162.54	-140.41	"
"	30	3.5323	"	-162.91	-140.41	"
"	35	3.5404	"	-163.28	-140.41	"
"	40	3.5485	"	-163.66	-140.42	"
"	45	3.5567	"	-164.04	-140.42	"

# Specific Conductance of non Aqueous Electrolytes

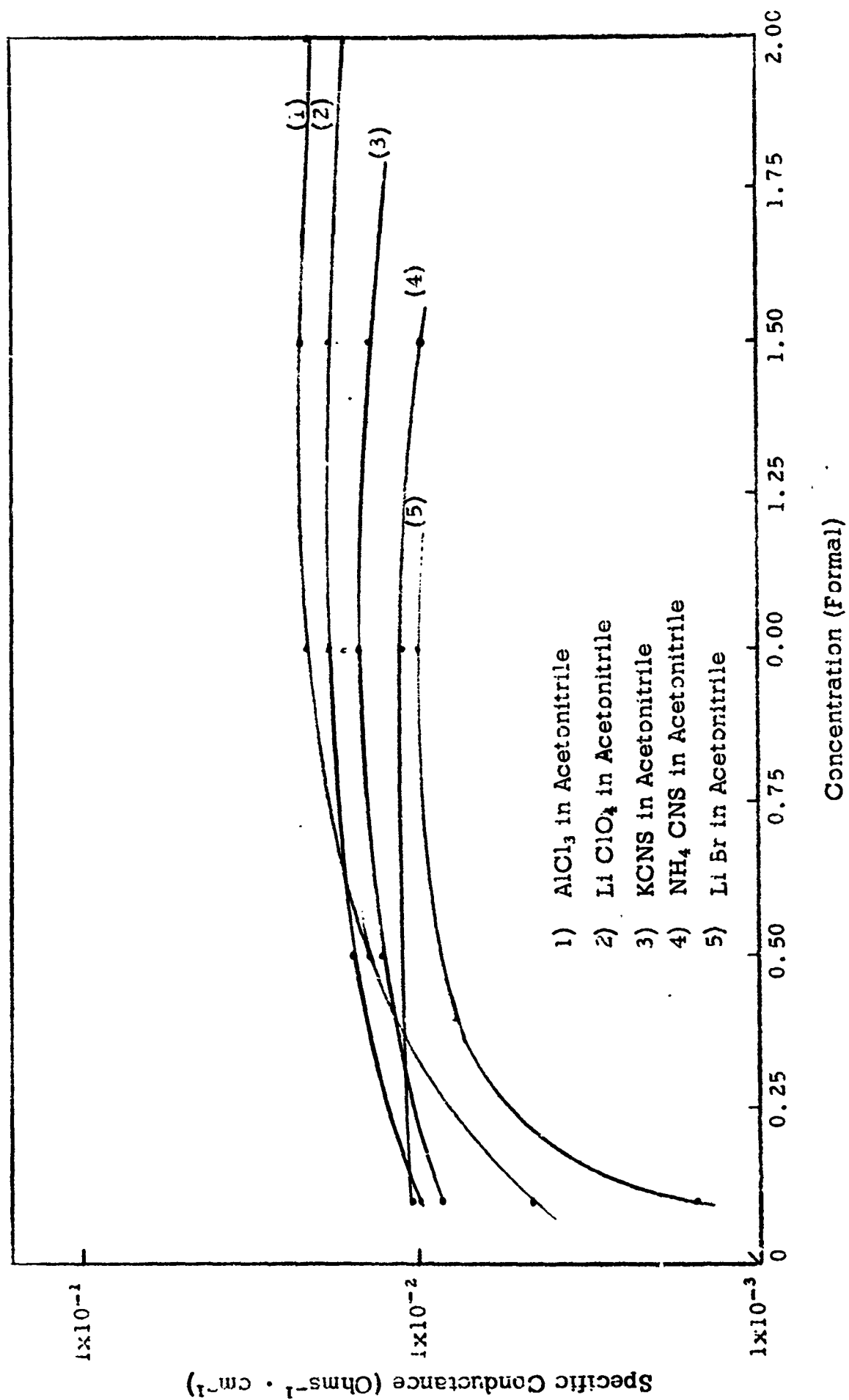


Figure 1

# Specific Conductance of Non Aqueous Electrolytes

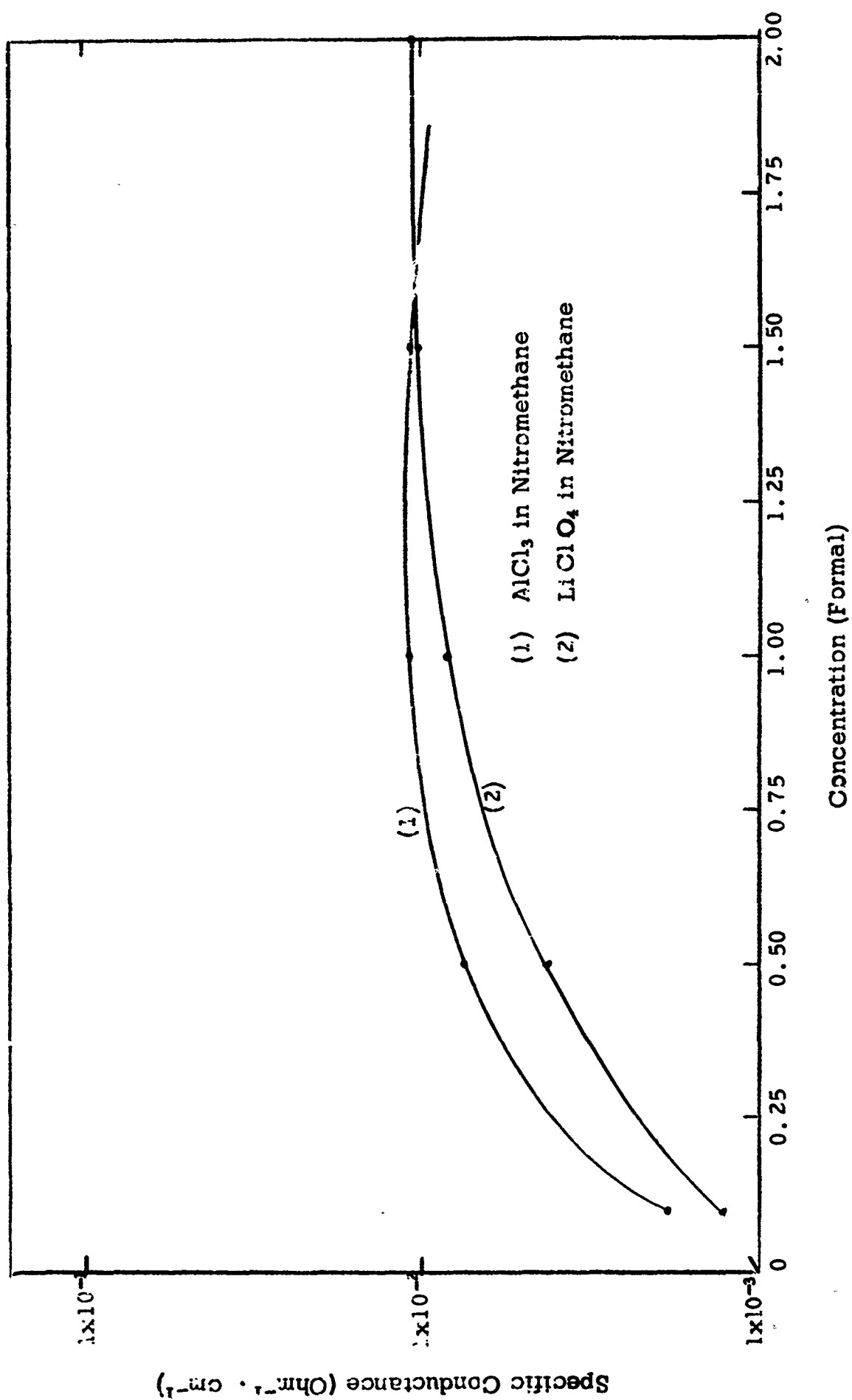


Figure 2



# Specific Conductance of Non Aqueous Electrolytes

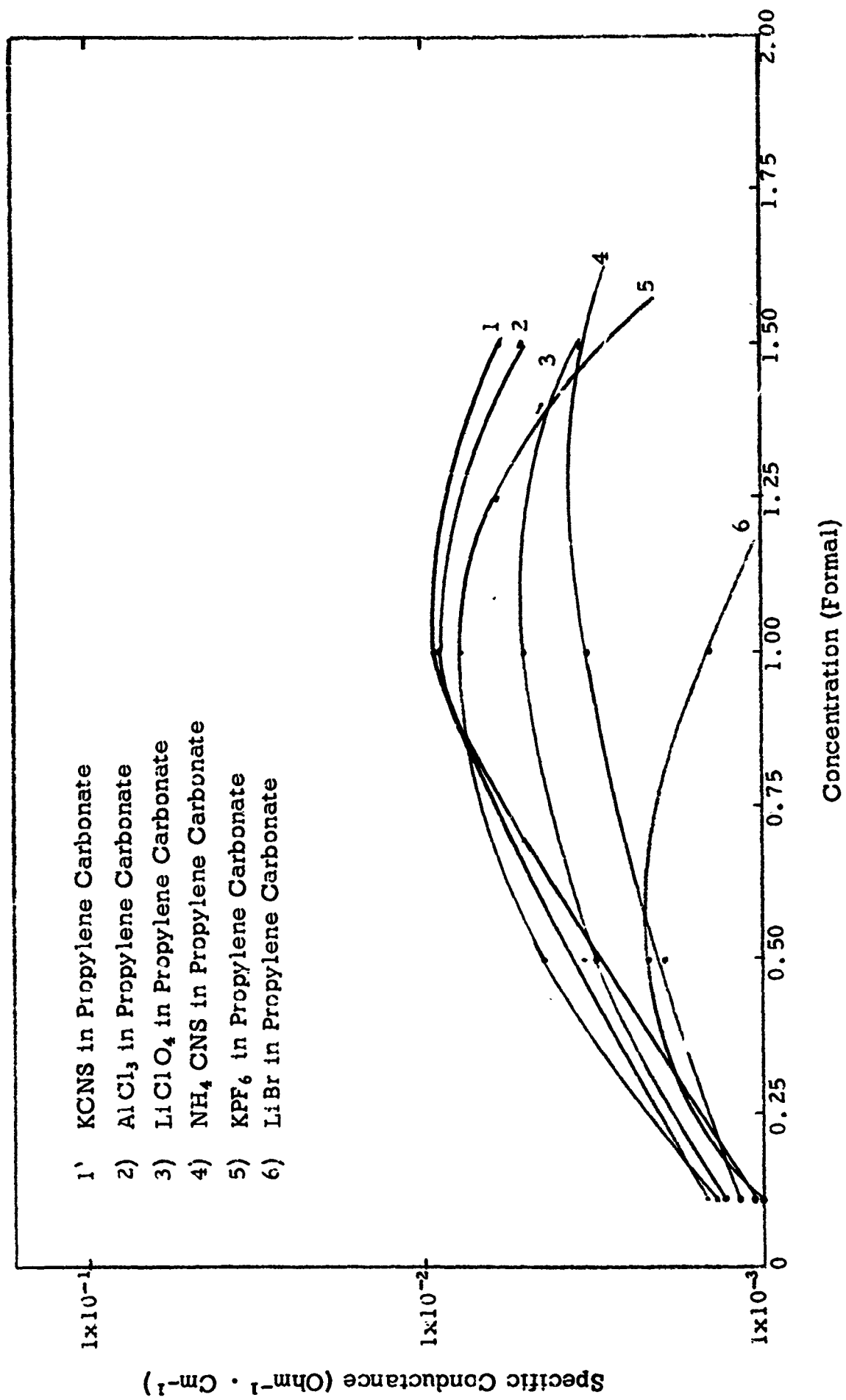


Figure 3

Figure 3

Specific Conductance of Non Aqueous Electrolytes

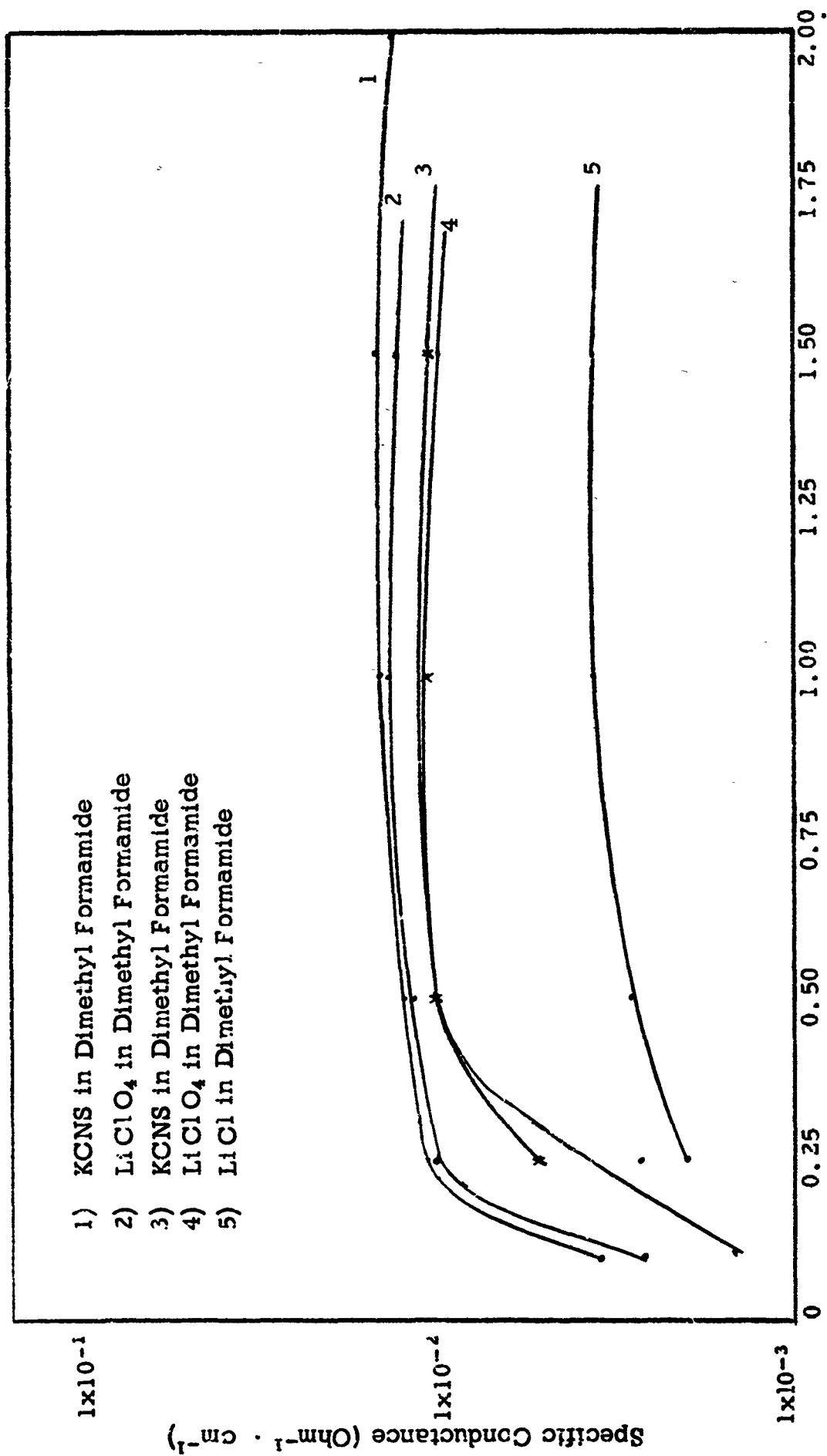


Figure 4

Shedlovsky Extrapolation Function

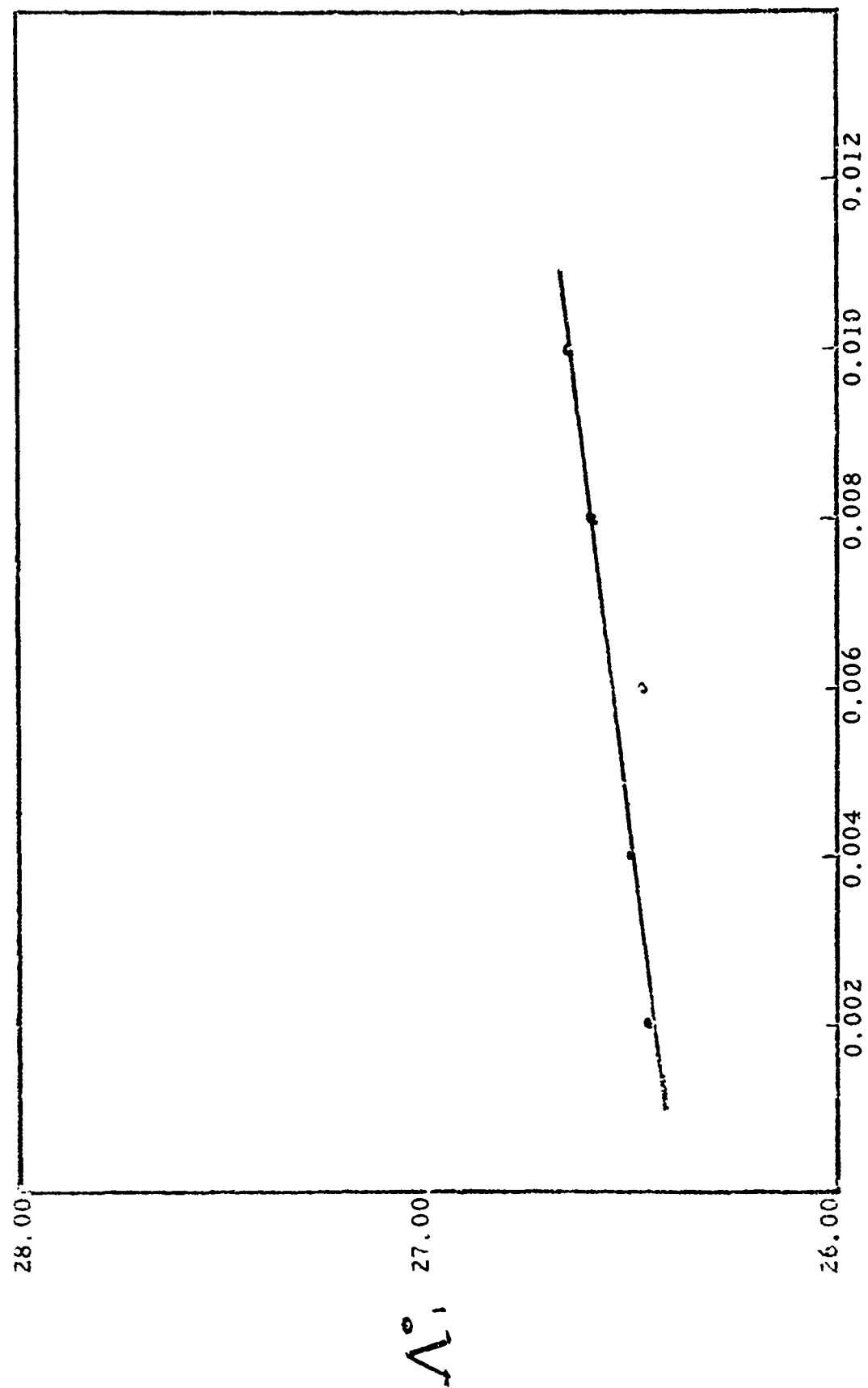


Figure 5

Concentration (Formal)

Determination of  $A_0$  and  $J$  for  $\text{LiClO}_4$  in Propylene Carbonate

Intercept =  $A_0 = 26.38$

Slope =  $J(A) = 47.915$

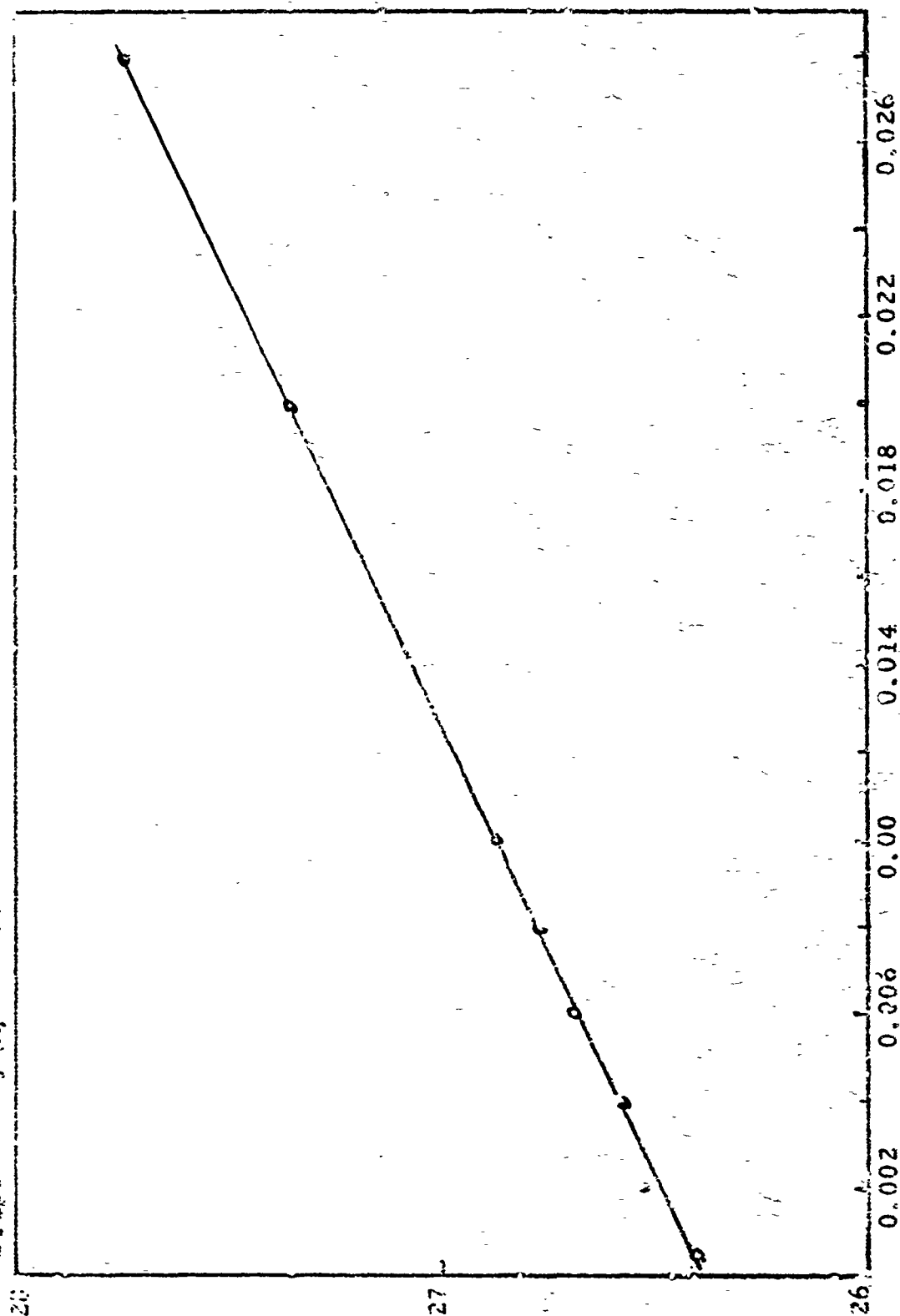


Figure 6

Determination of  $\lambda^\circ$  from J (A)

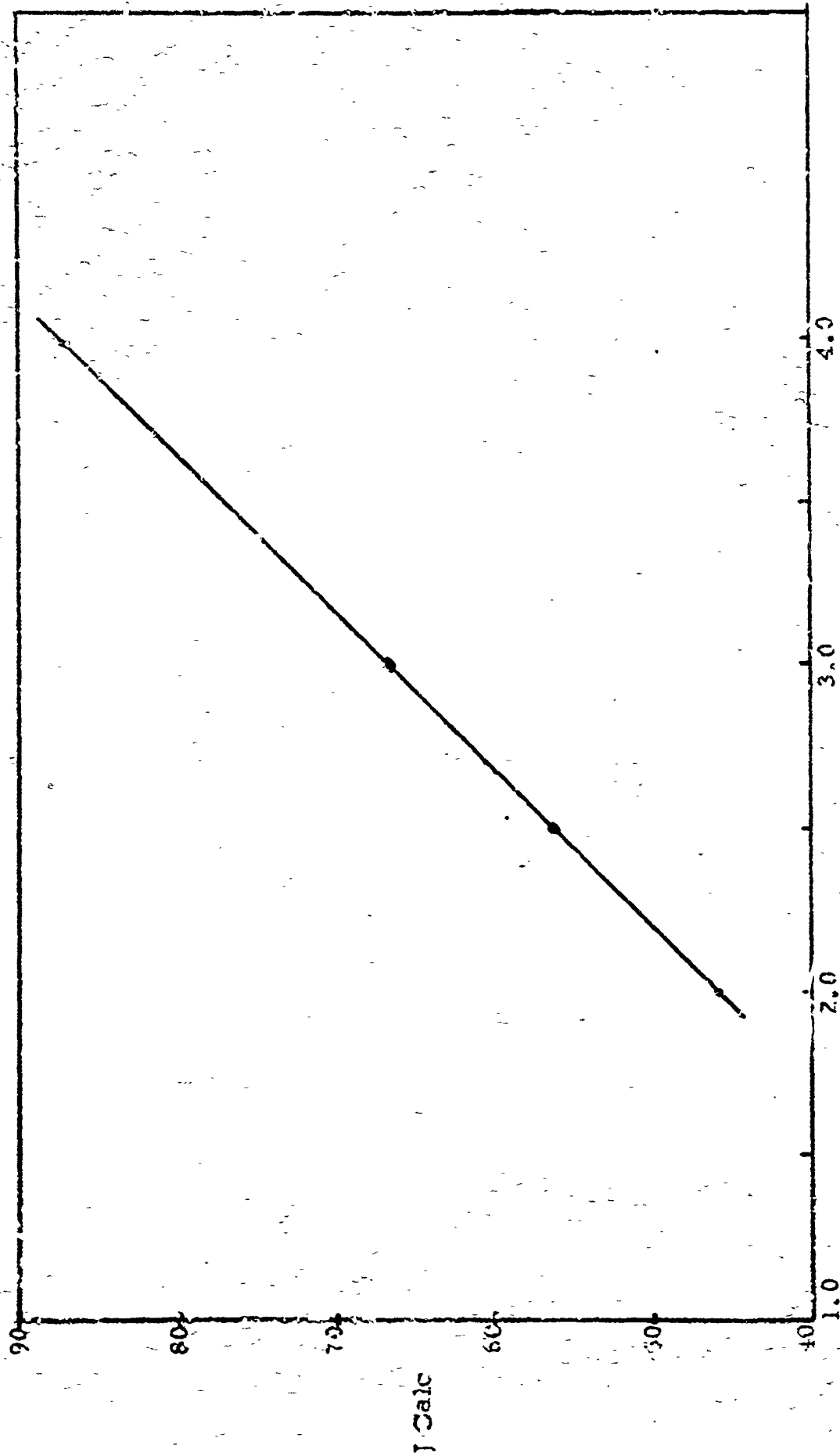


Figure 7

$\lambda^\circ$  (Angstroms)

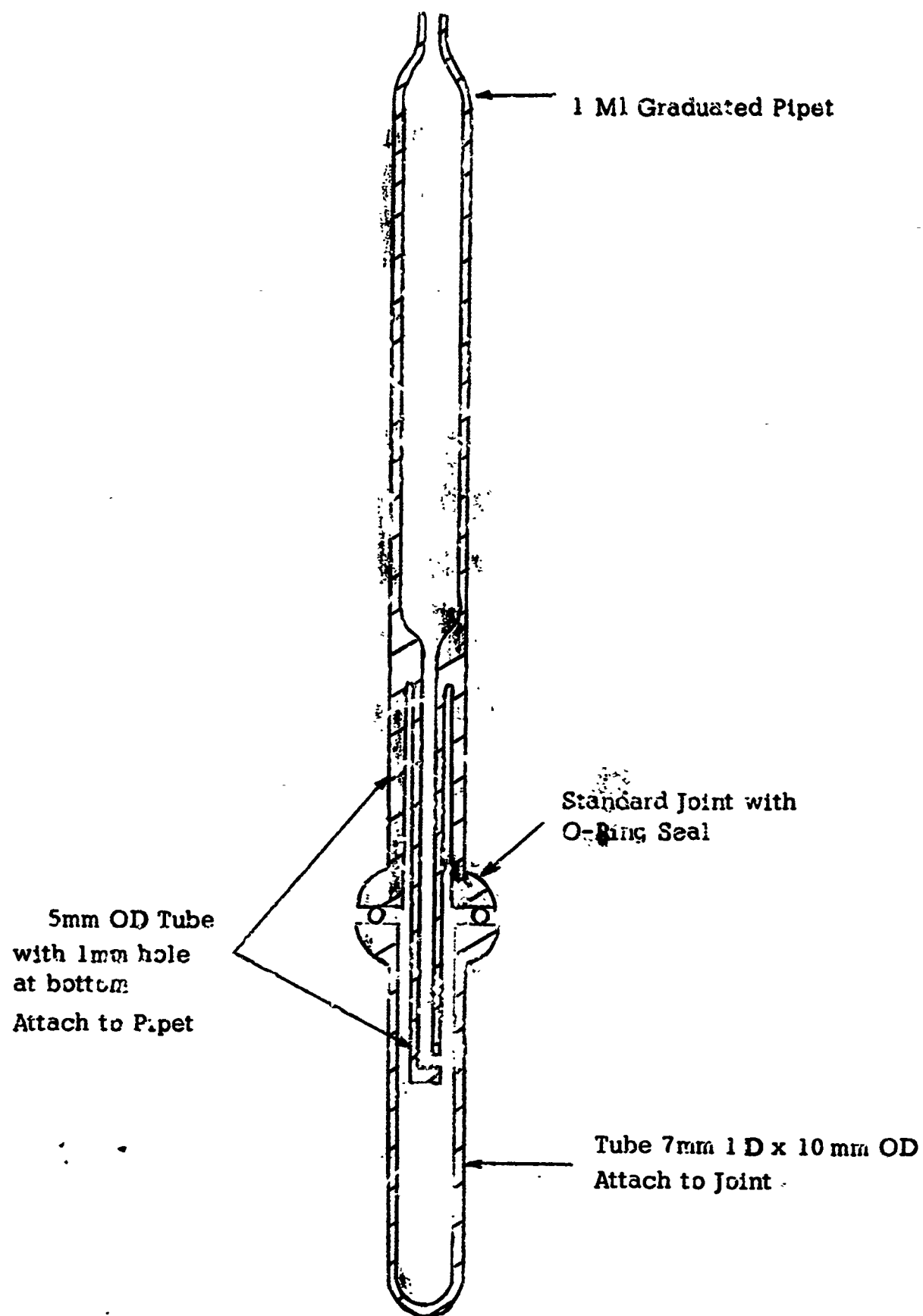
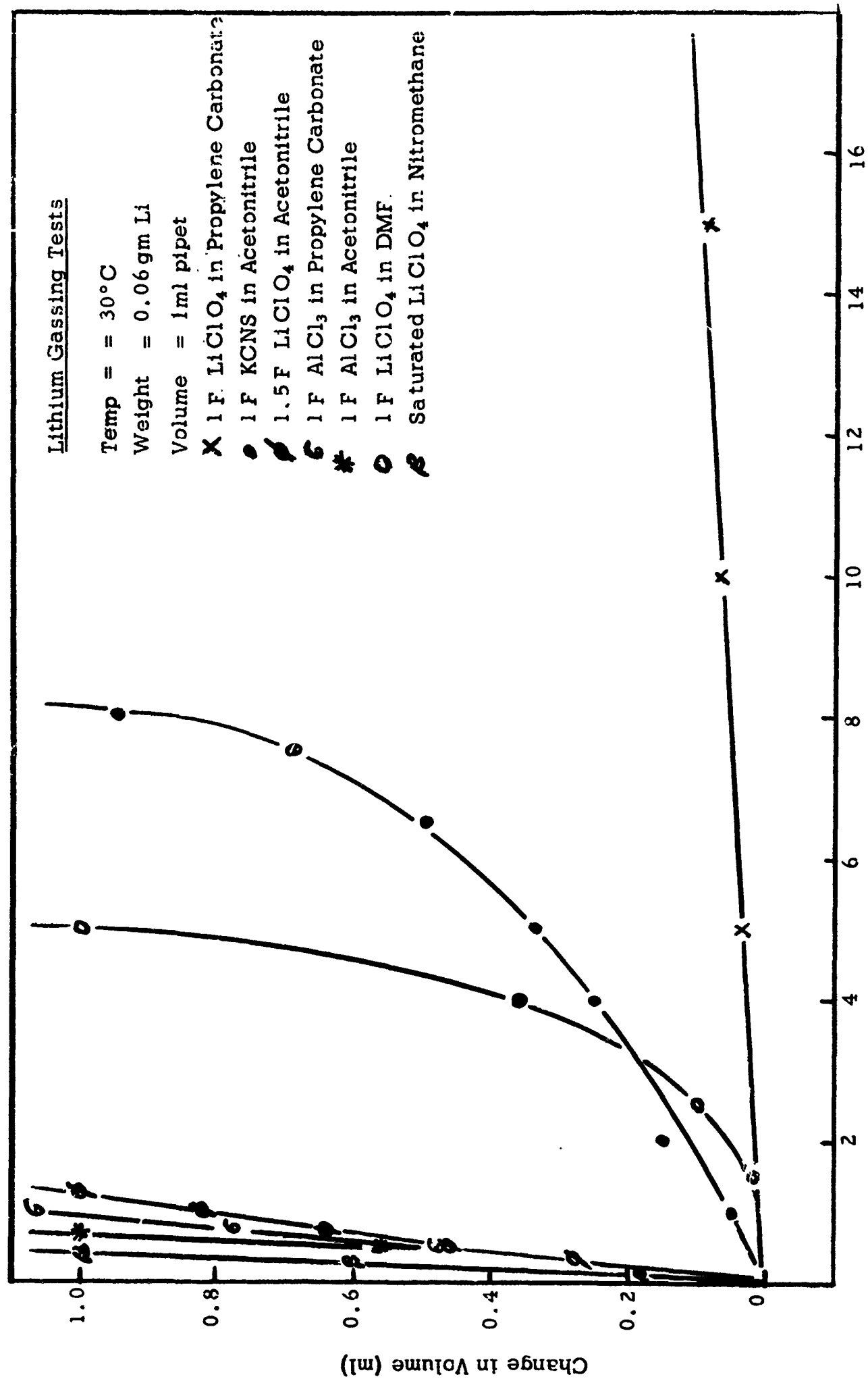


Figure 8



Time Elapsed (hours)

Figure 9

## Reference Electrode Cell

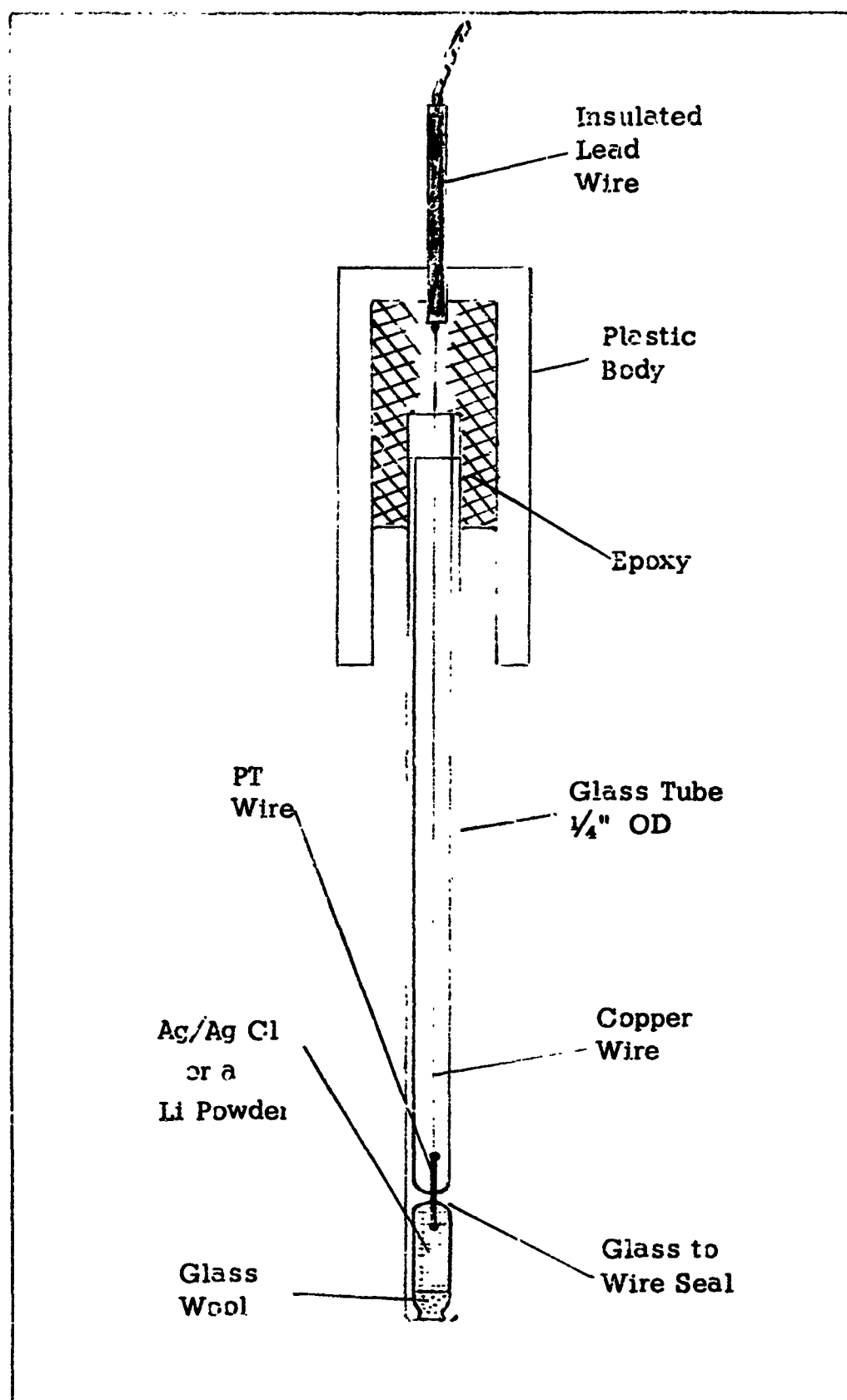


Figure 10



# Lithium Reference Electrode

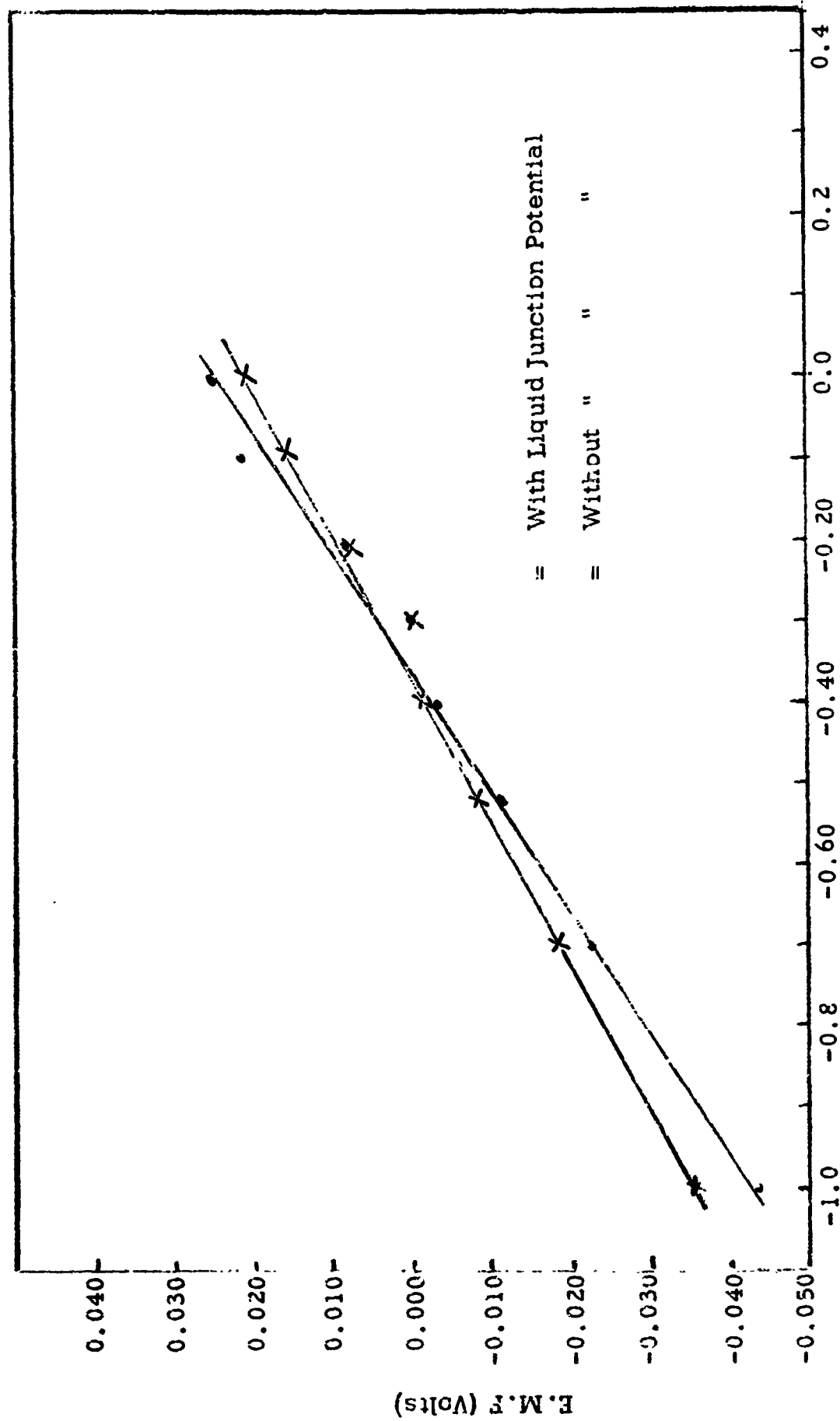


Figure 11  $\text{Log}_{10} C_2$

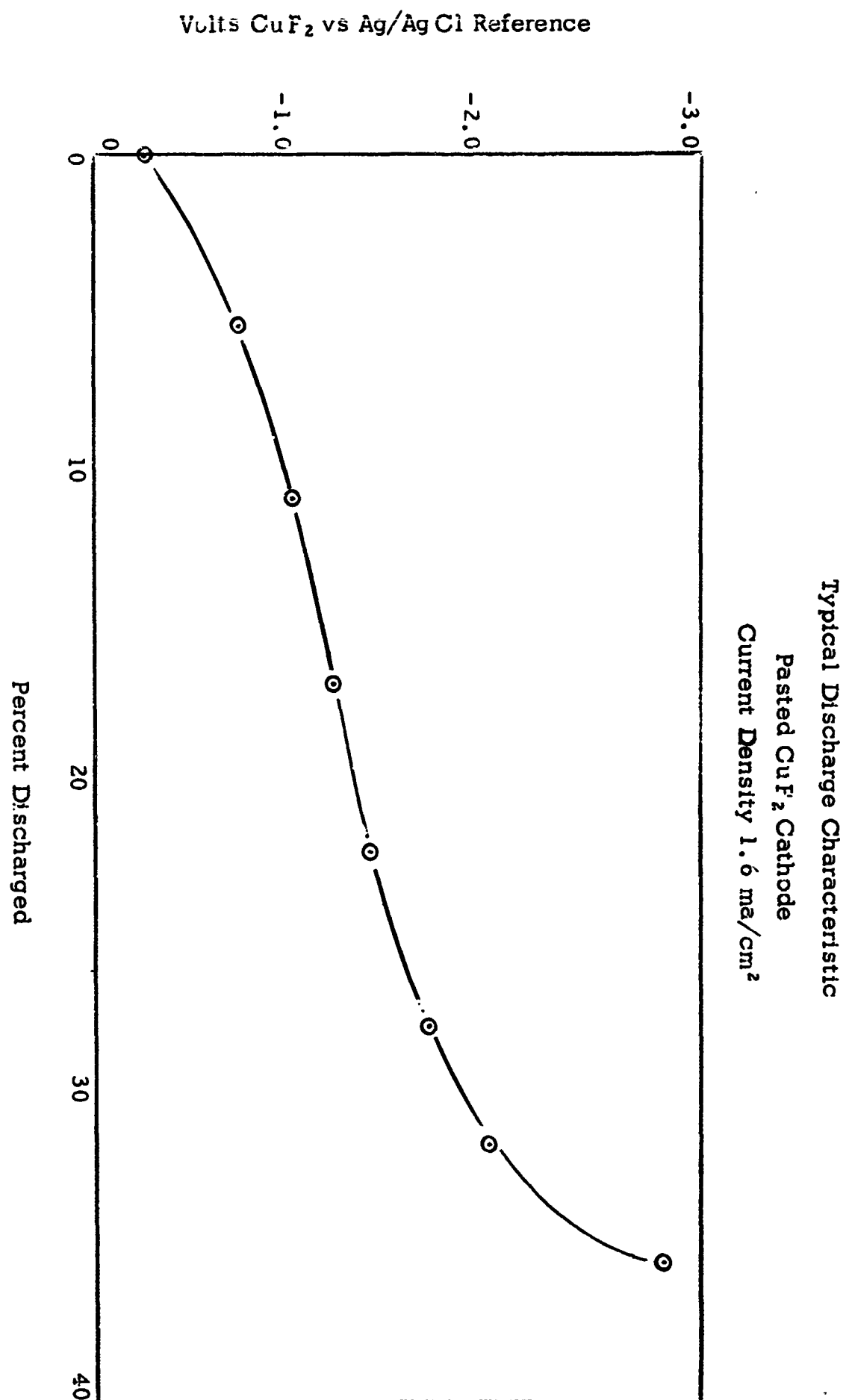


Figure 12

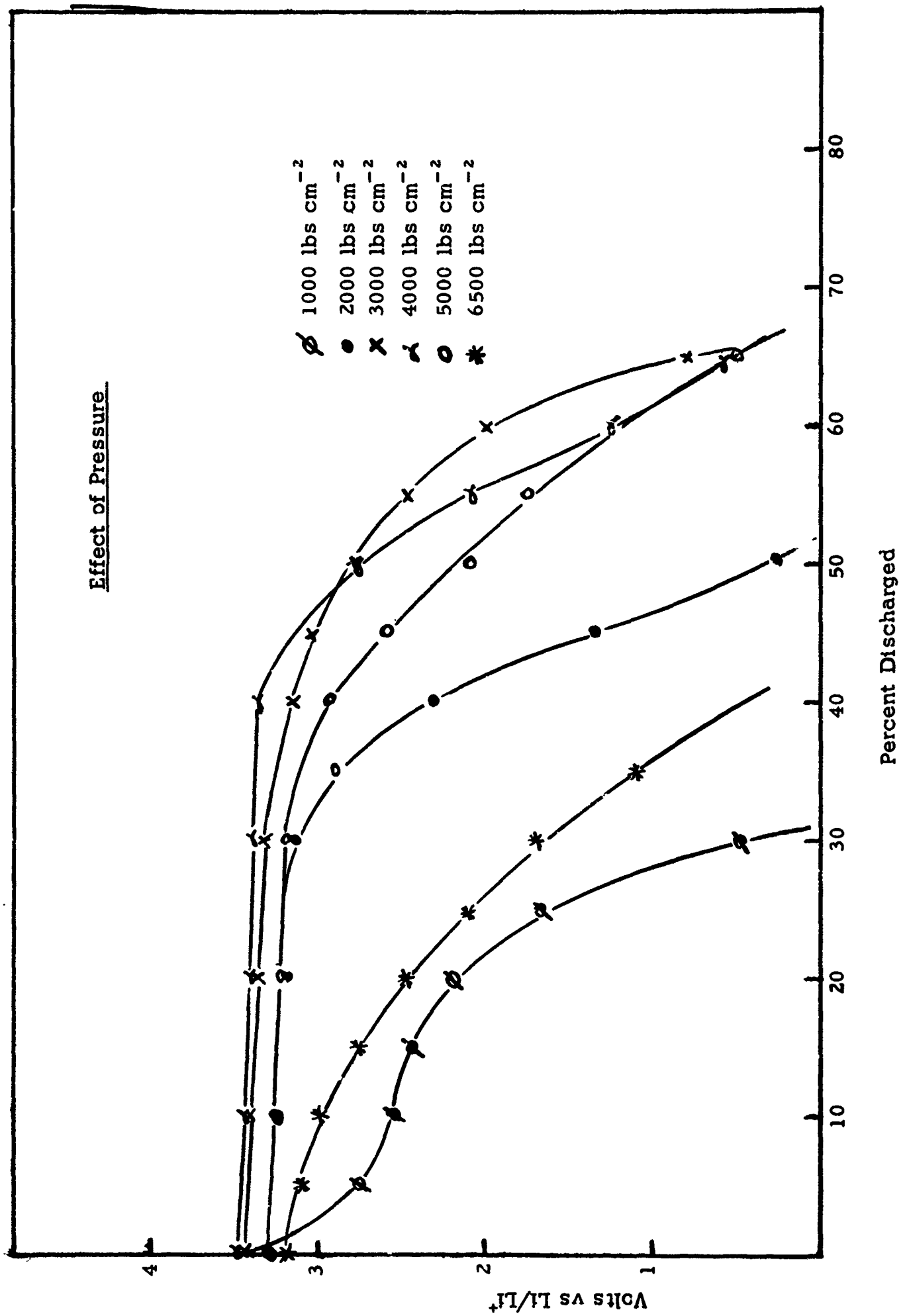


Figure 13

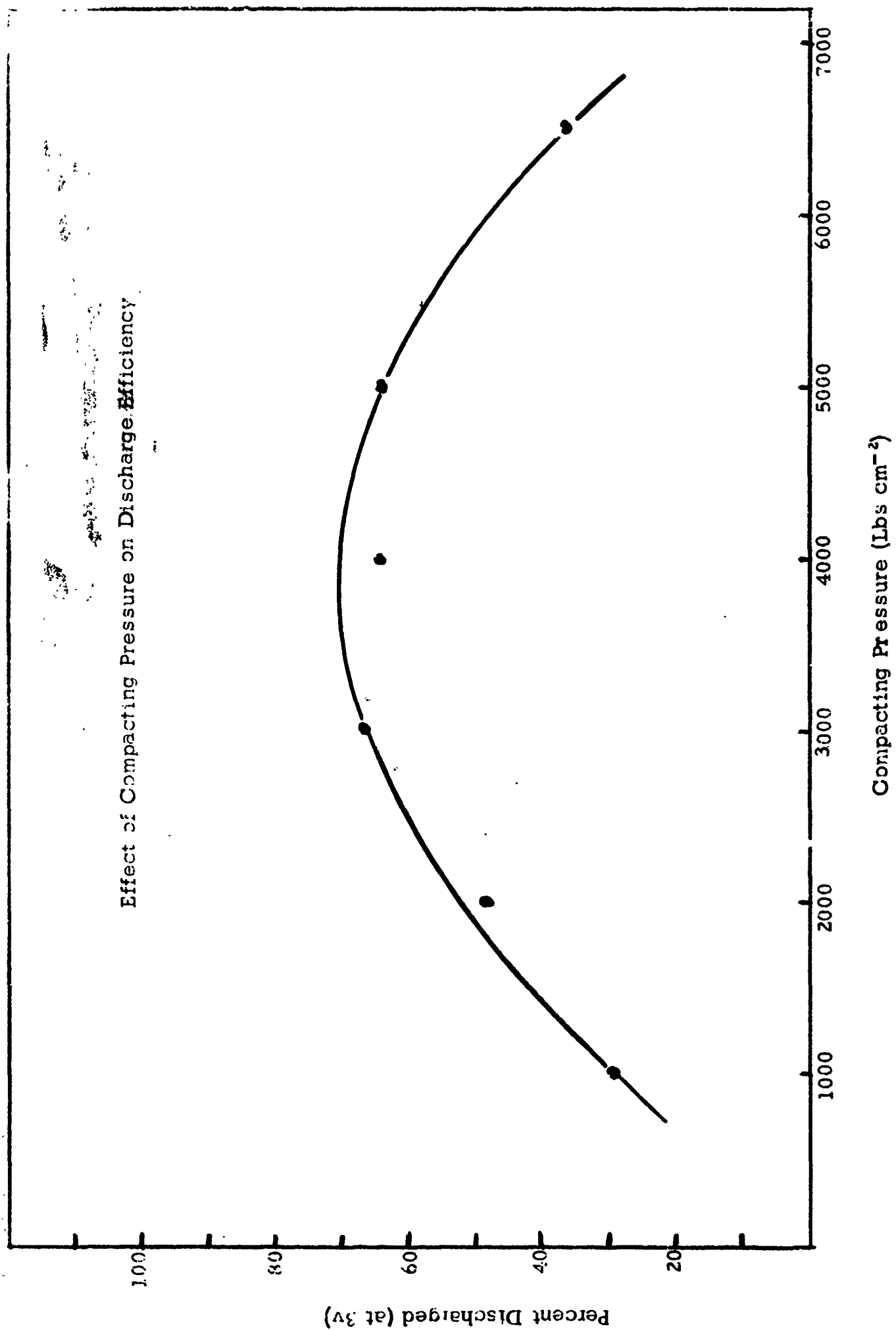
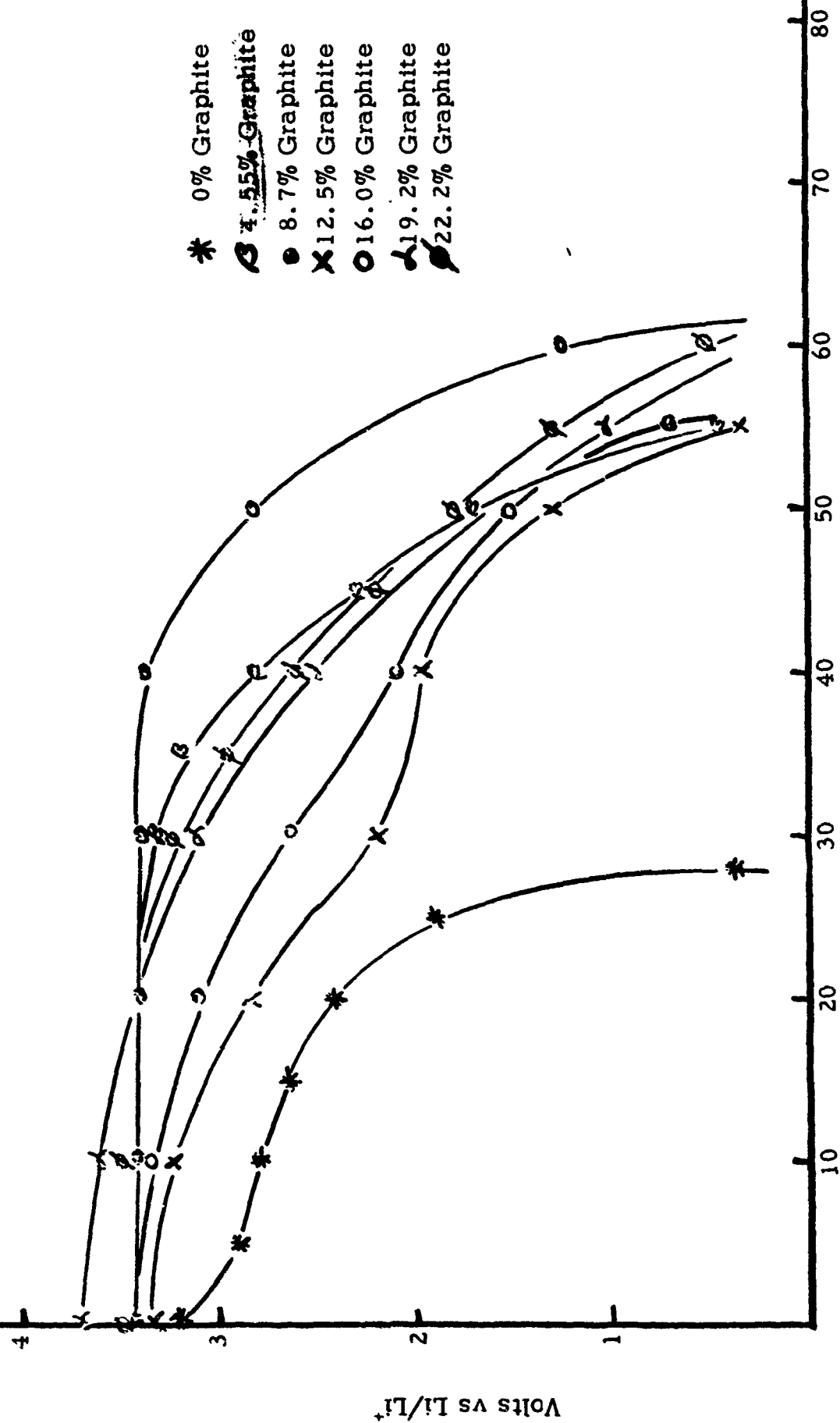


Figure 14

Effect of Graphite Concentration on Performance



Percent Discharged

Figure 15

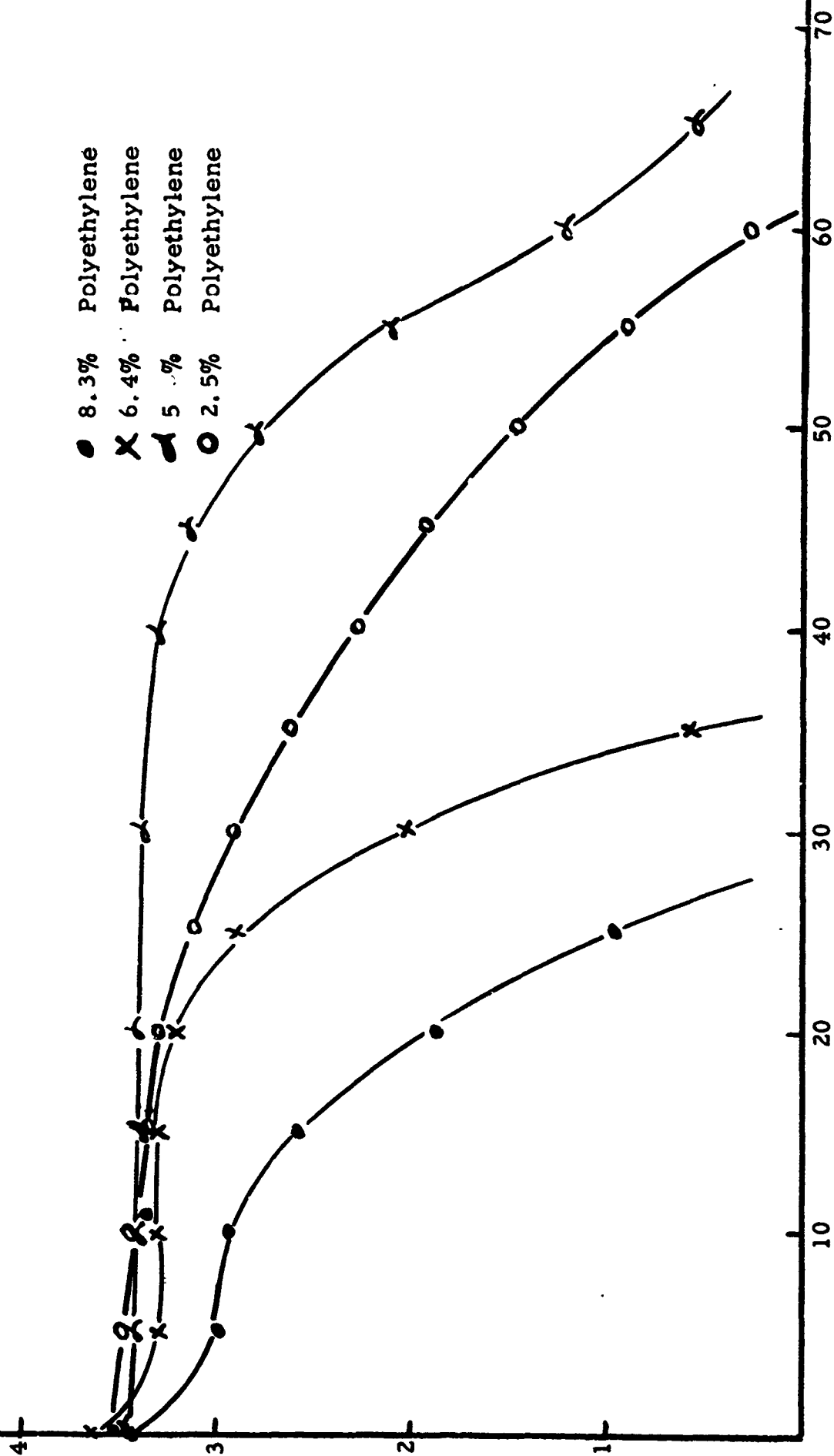
Effect of Amount of Binder on Performance

- 8.3% Polyethylene
- × 6.4% Polyethylene
- ⧻ 5% Polyethylene
- 2.5% Polyethylene

Volts vs Li/Li<sup>+</sup>

Percent Discharged

Figure 16



Effect of Particle Size of  
CuF<sub>2</sub> on Performance

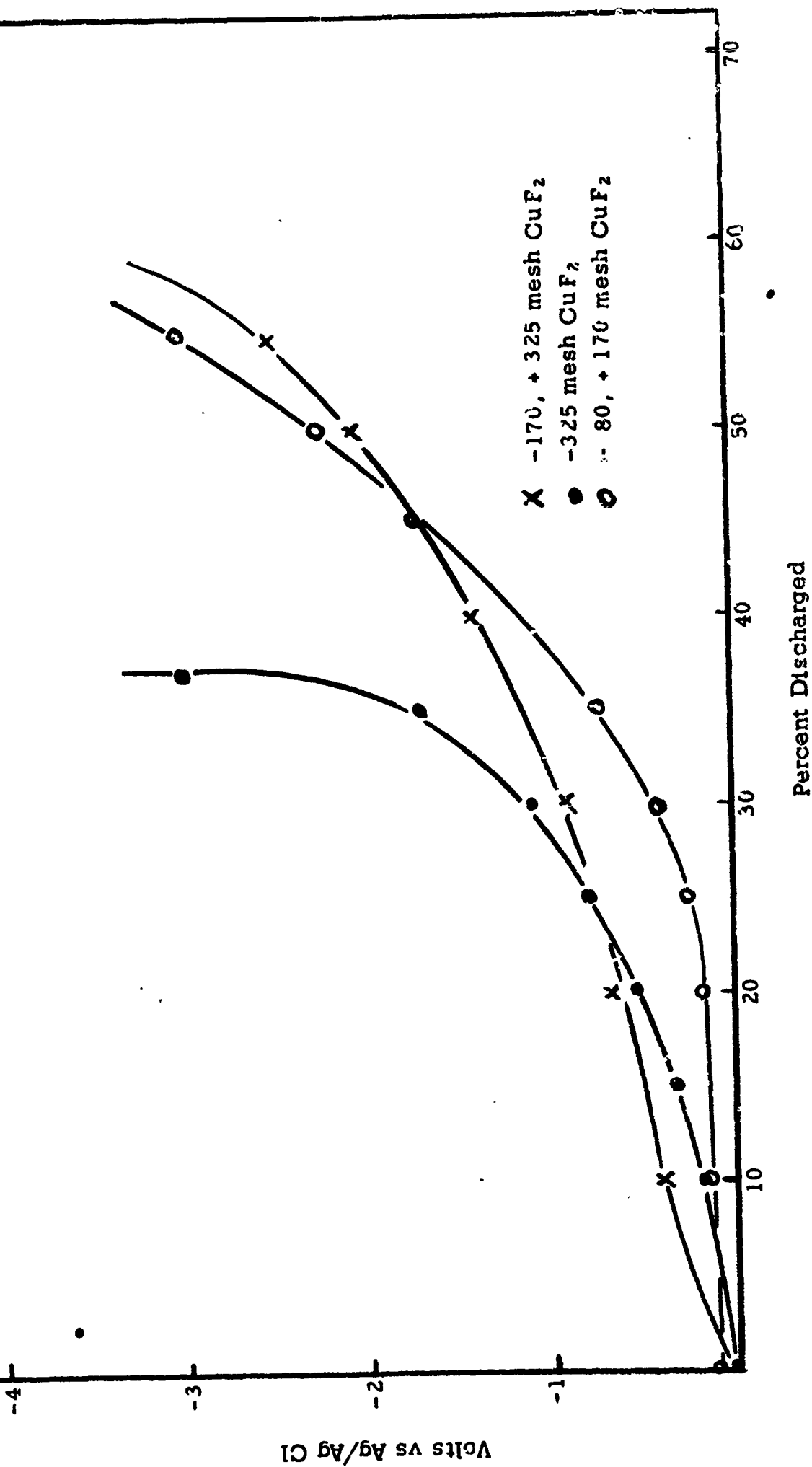


Figure 17

Discharge of  $\text{CuF}_2$  Electrode in Dimethyl Sulfoxide

Electrolyte =  $1\text{F LiClO}_4$  in DMSO

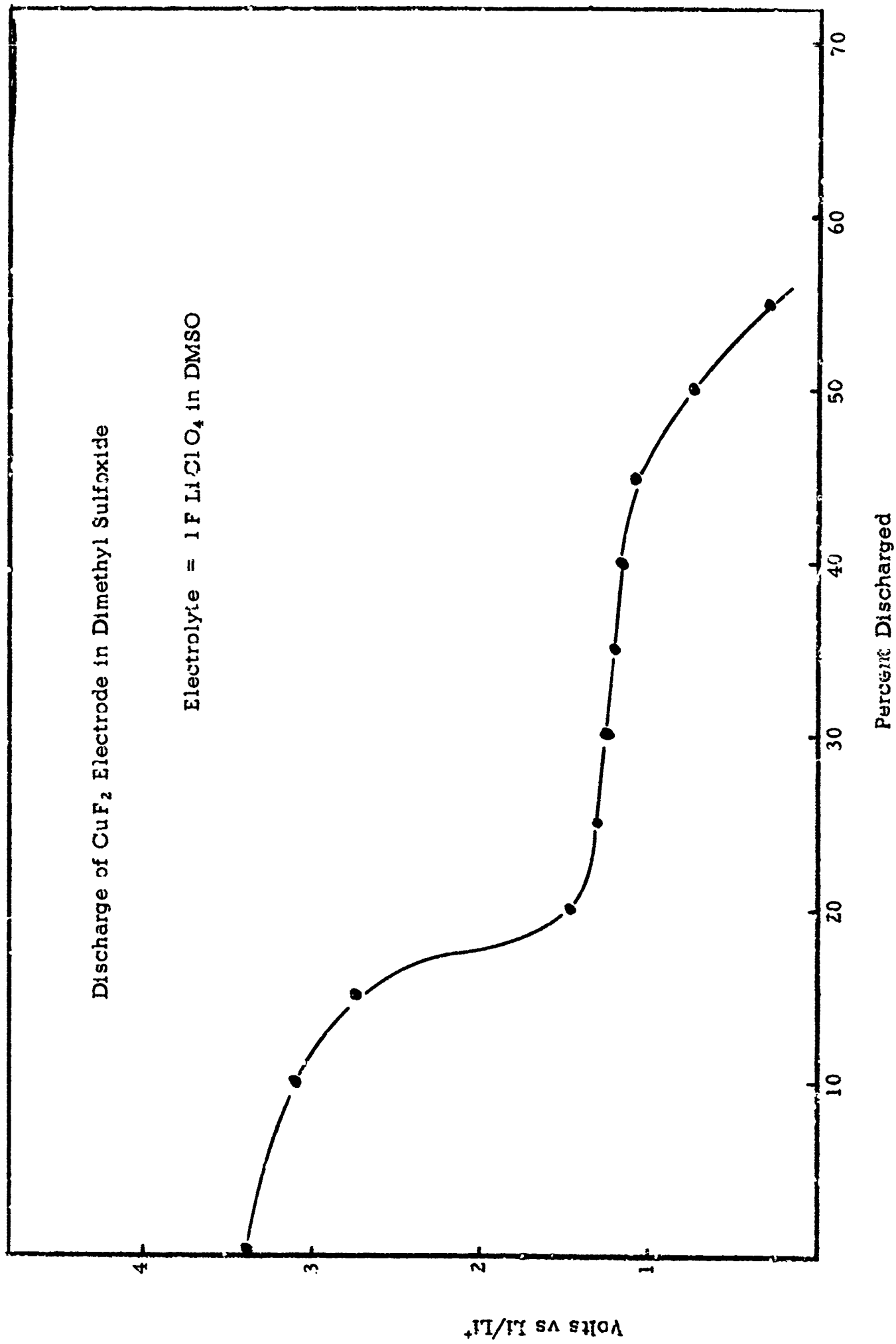


Figure 18



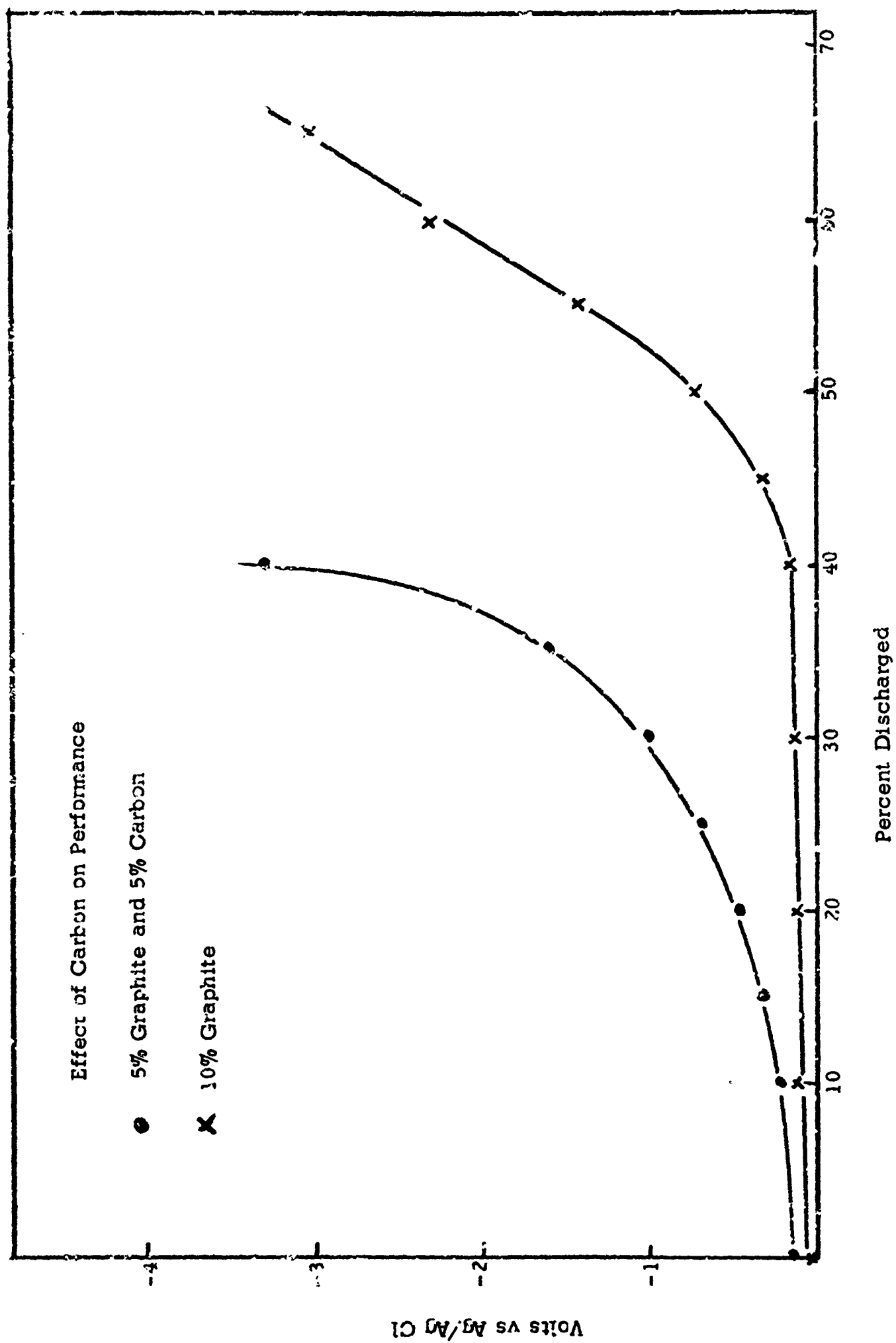


Figure 19

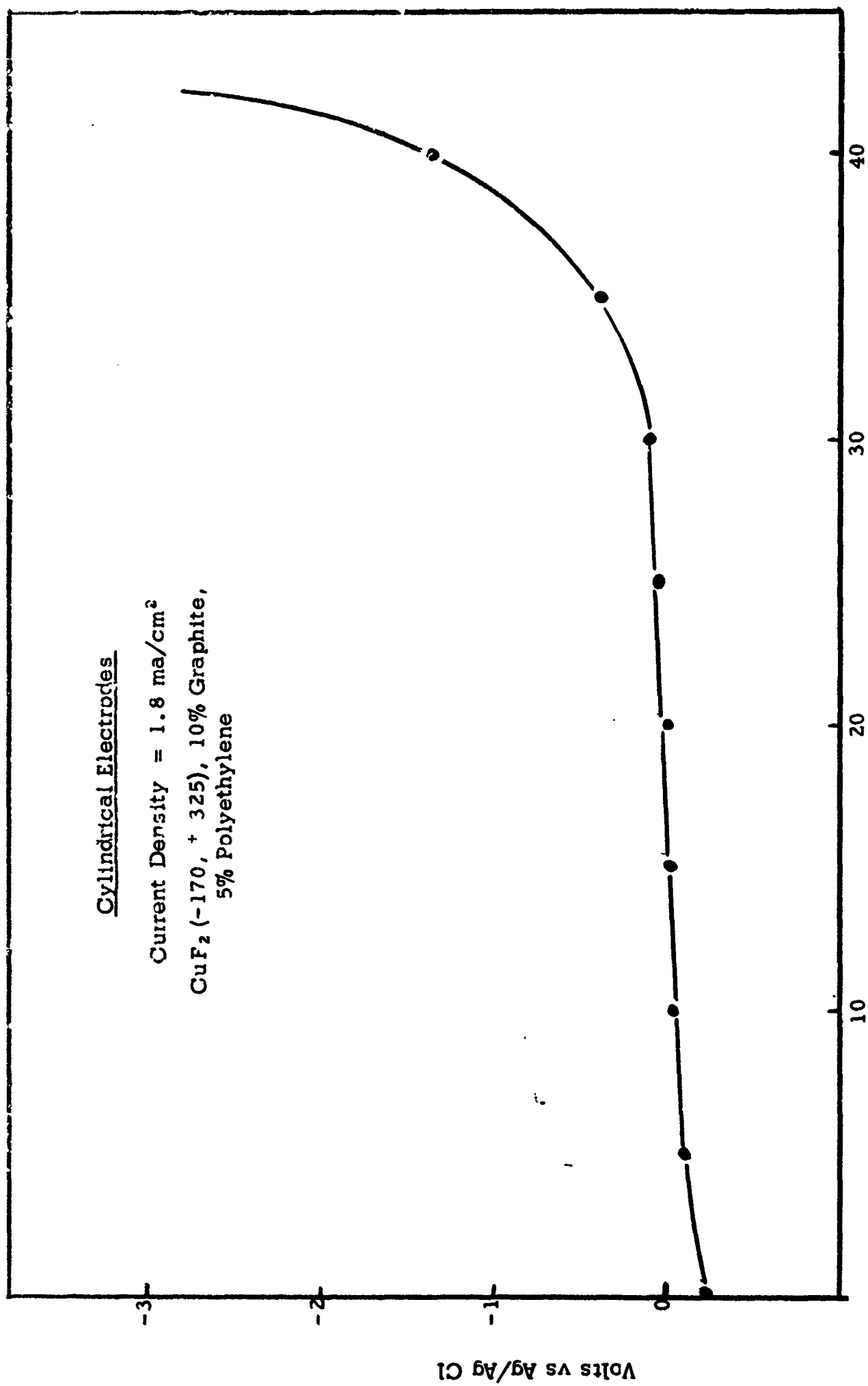


Figure 20

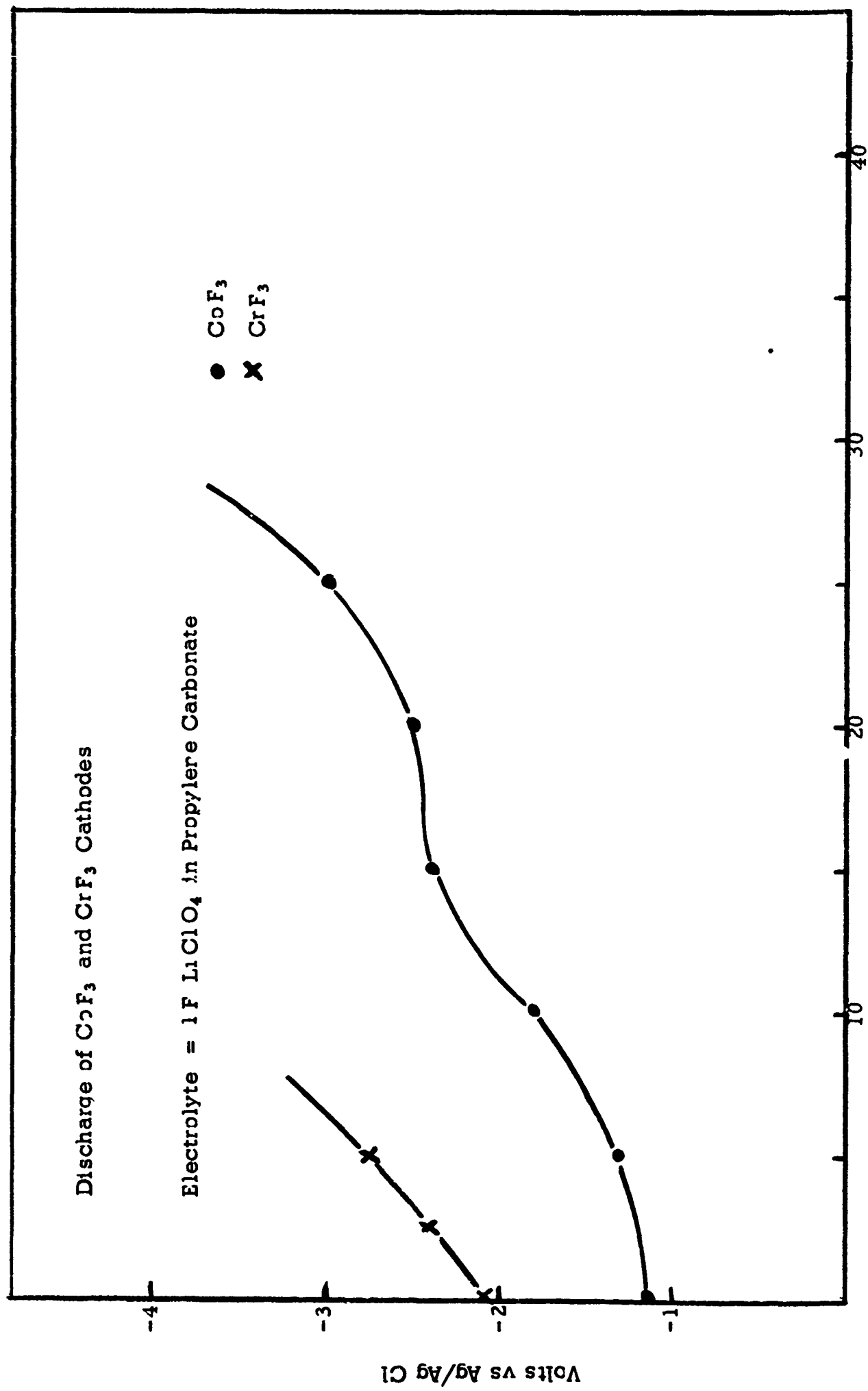


Figure 21

# Cell Voltage vs Temperature

## Lithium - Cupric Fluoride Cell

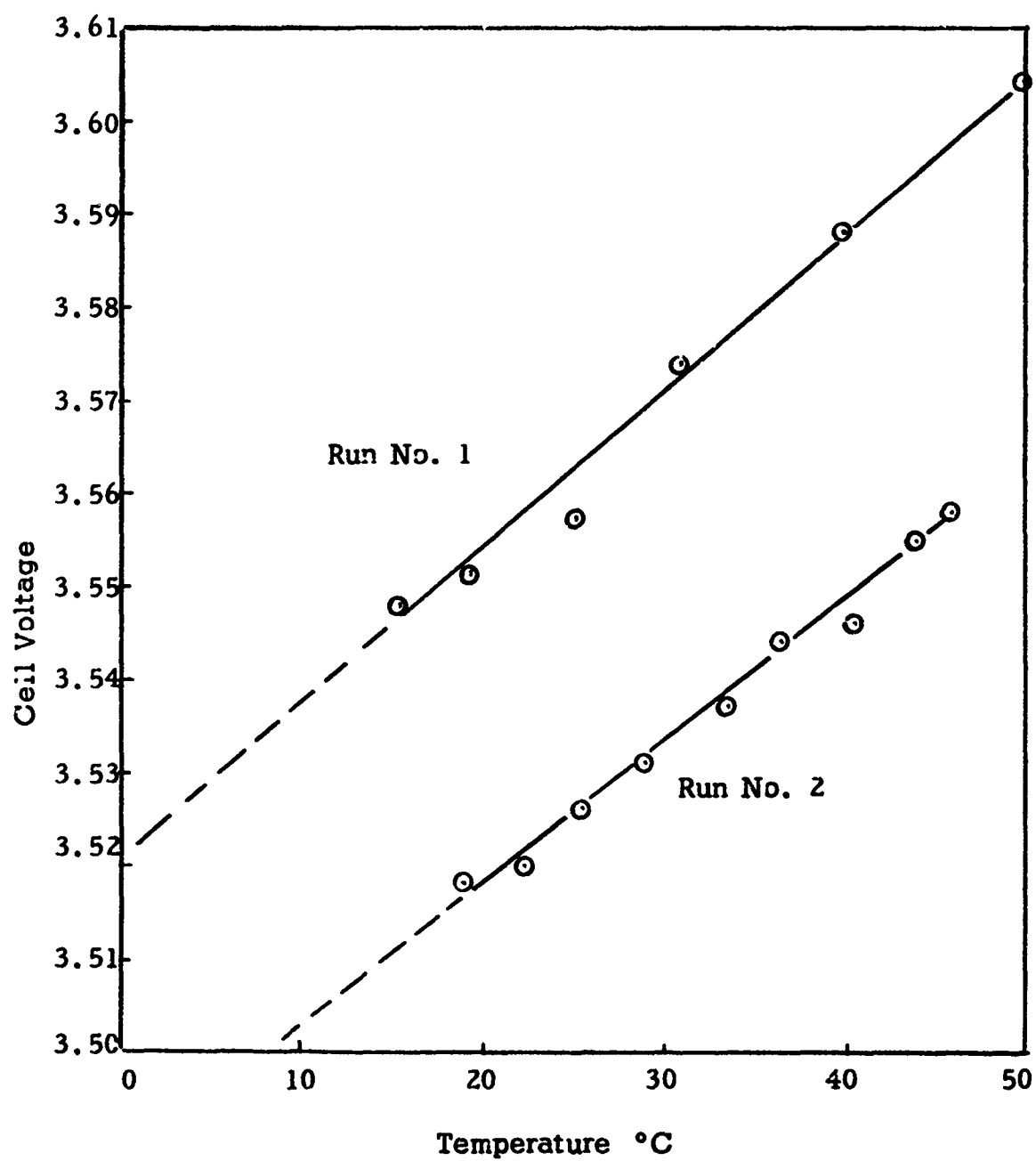


Figure 22

$\Delta G$  vs Temperature  
Lithium Cupric Fluoride Cell

Reaction:  $2 \text{Li} + \text{CuF}_2 \rightleftharpoons 2 \text{LiF} + \text{Cu}$

Literature Value  $\Delta G_{25^\circ\text{C}} = 163 \text{ KCAL}$

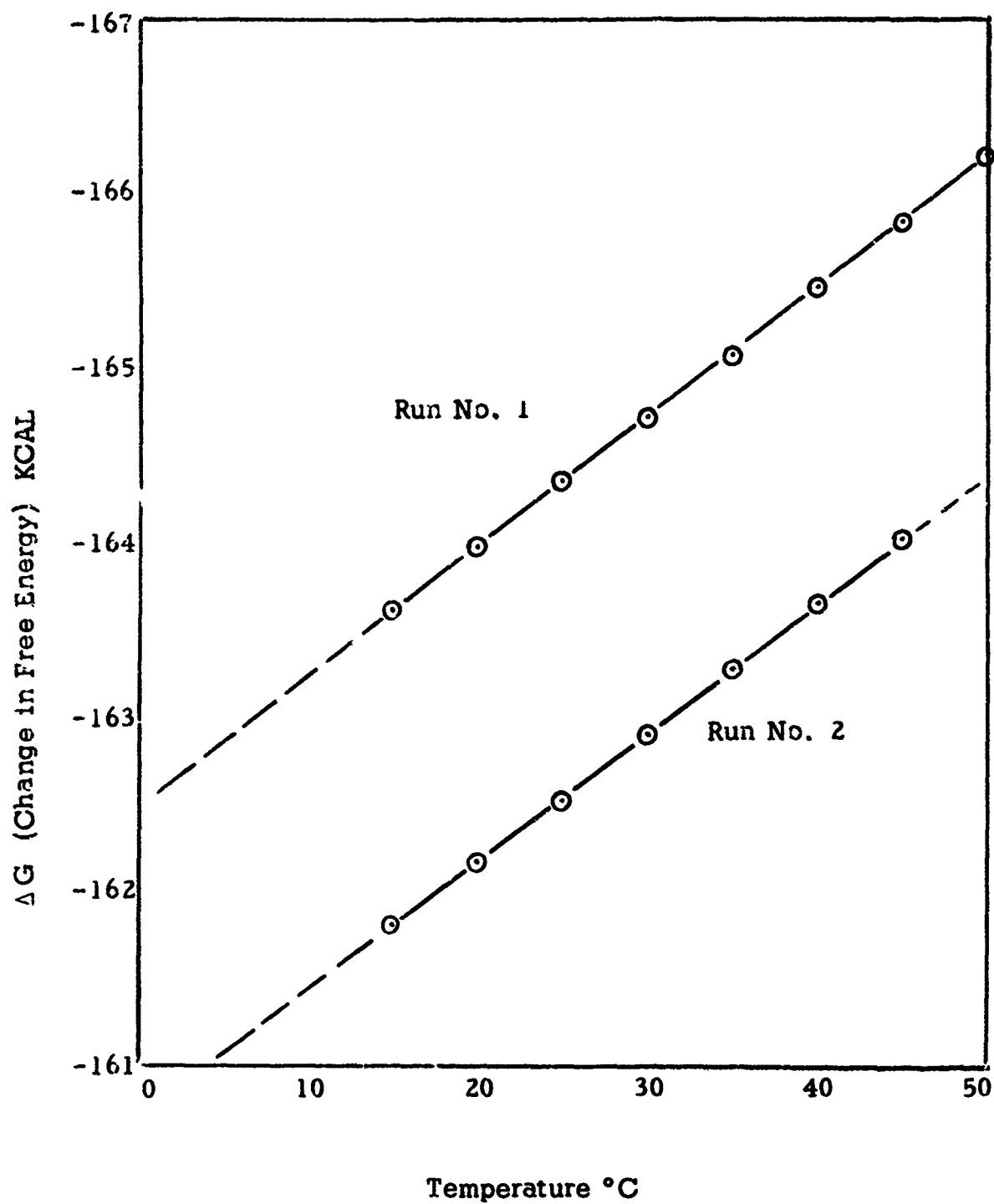
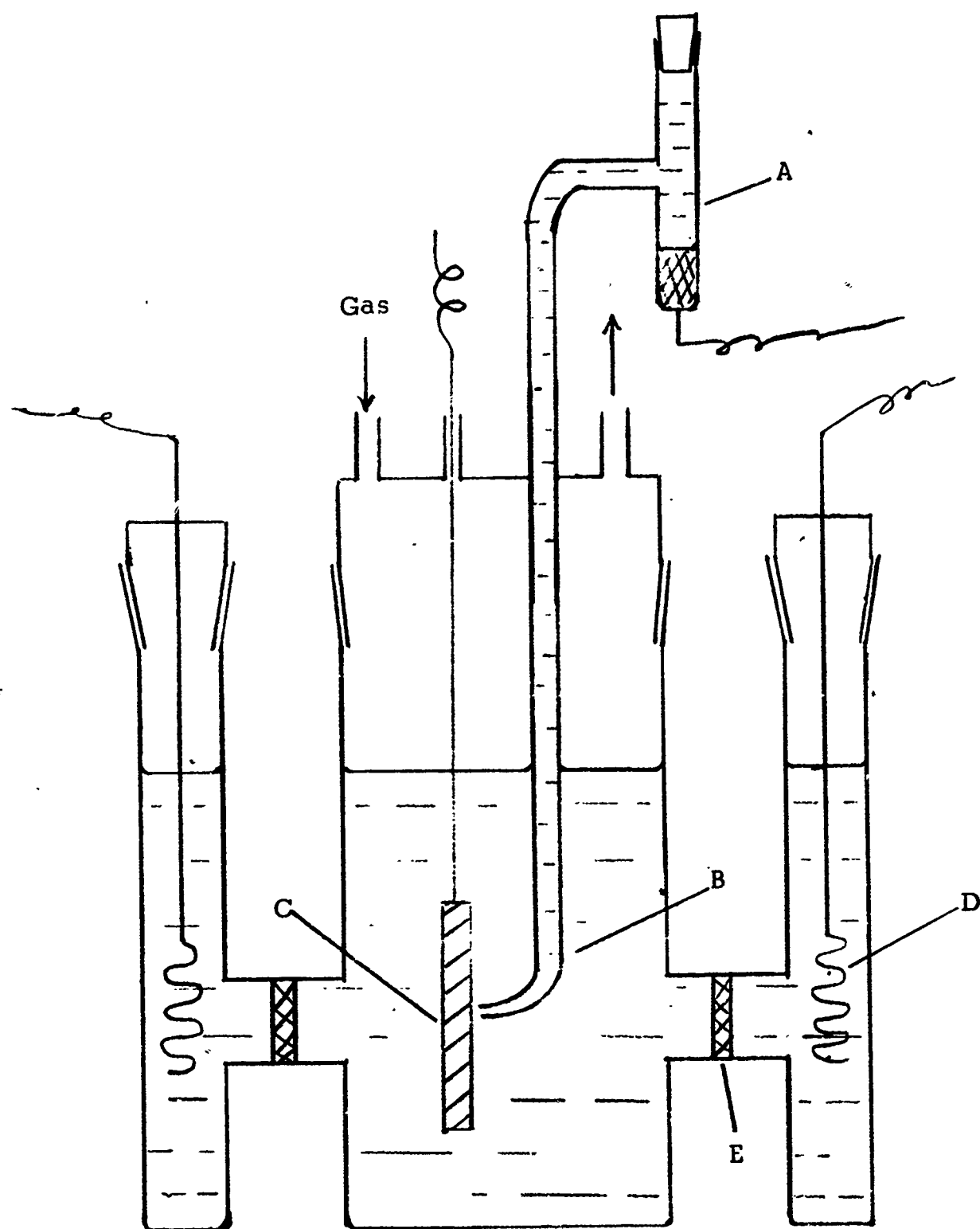


Figure 23

# Electrode Test Cell



Code

Figure 24

- A - Reference Electrode
- B - Luggin Capillary
- C - Working Electrode
- D - Platinum Counter Electrode
- E - Fritted Glass Plug

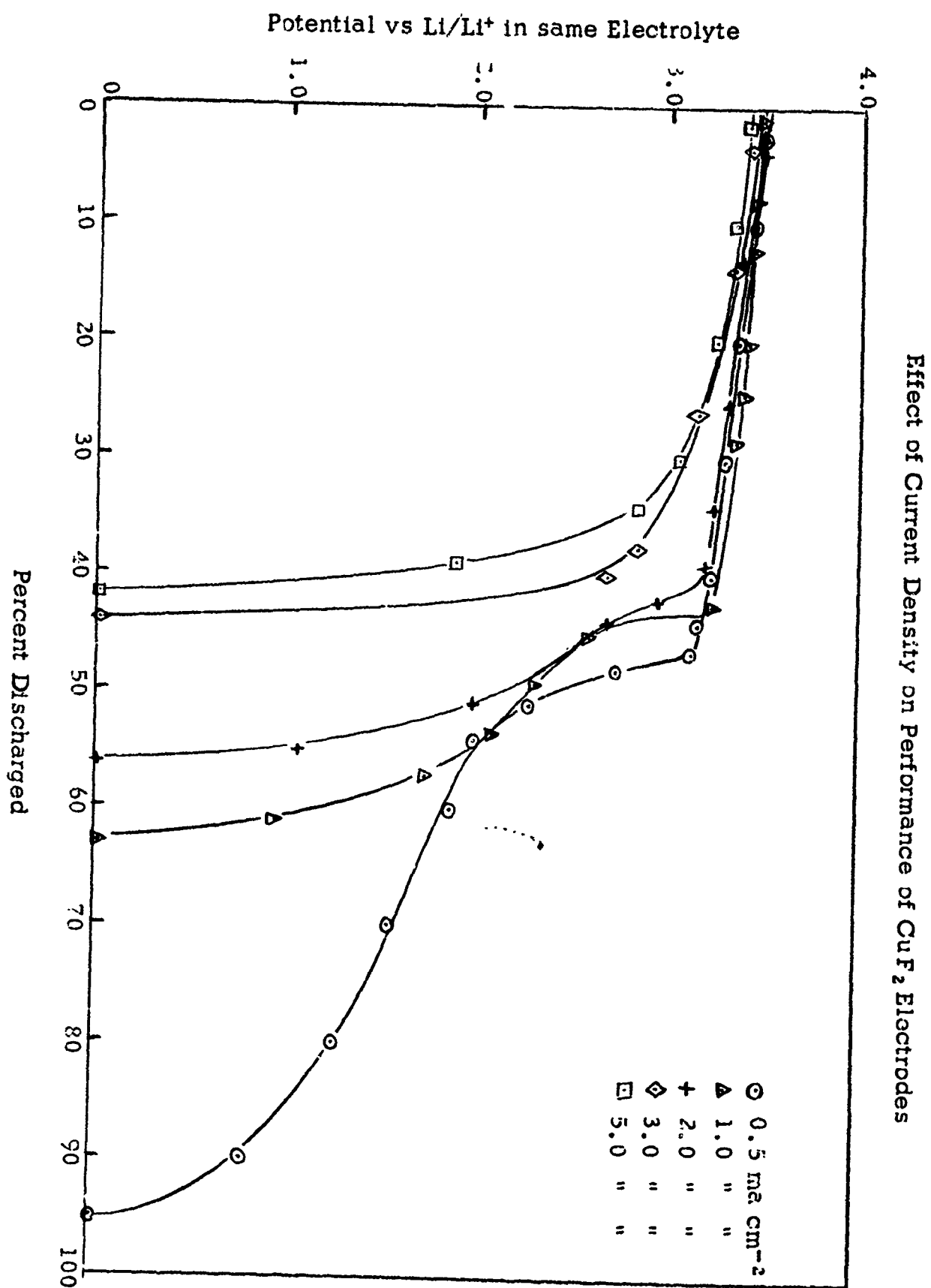


Figure 25

# Polarization of Cupric Fluoride Electrode

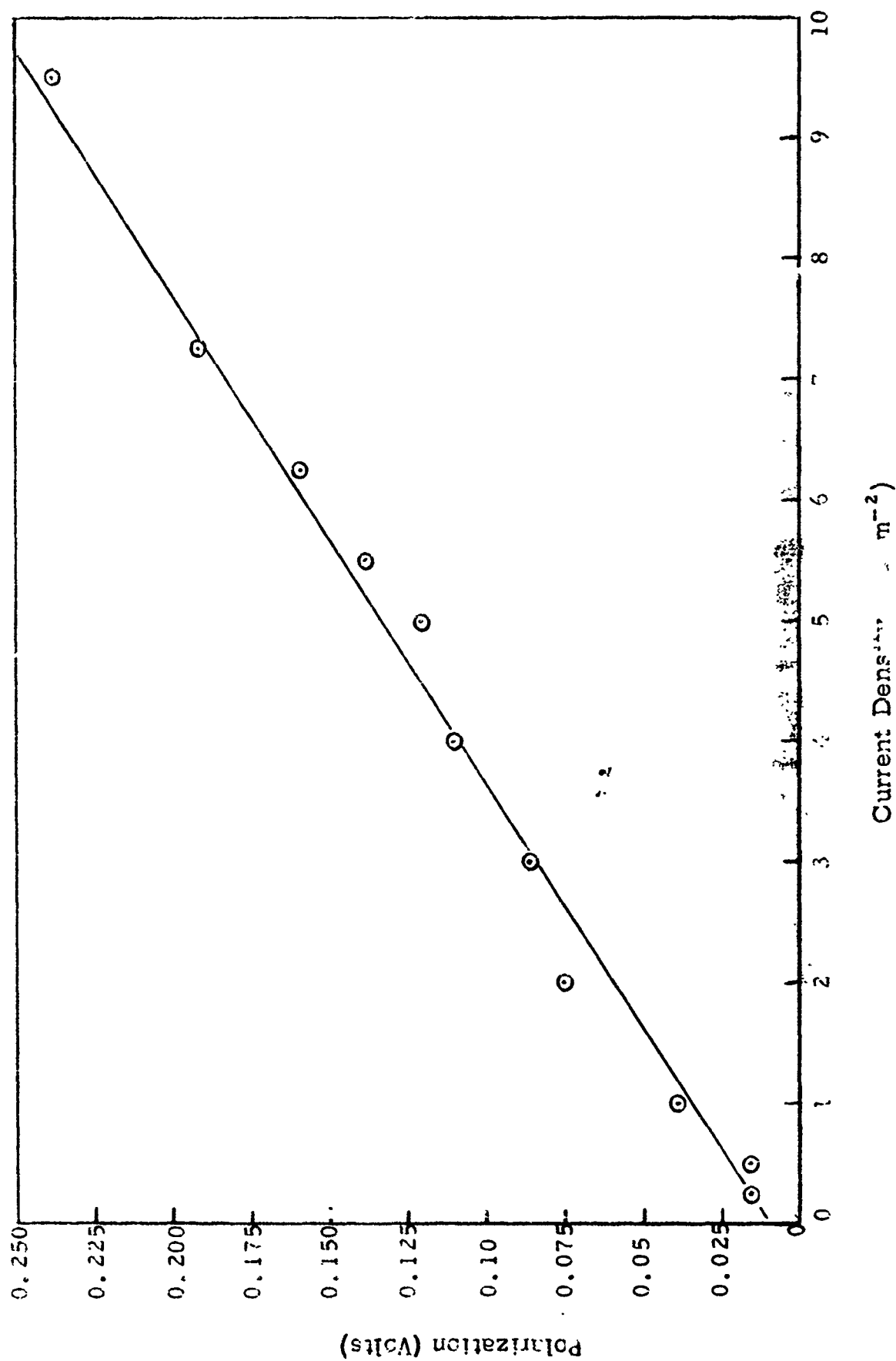
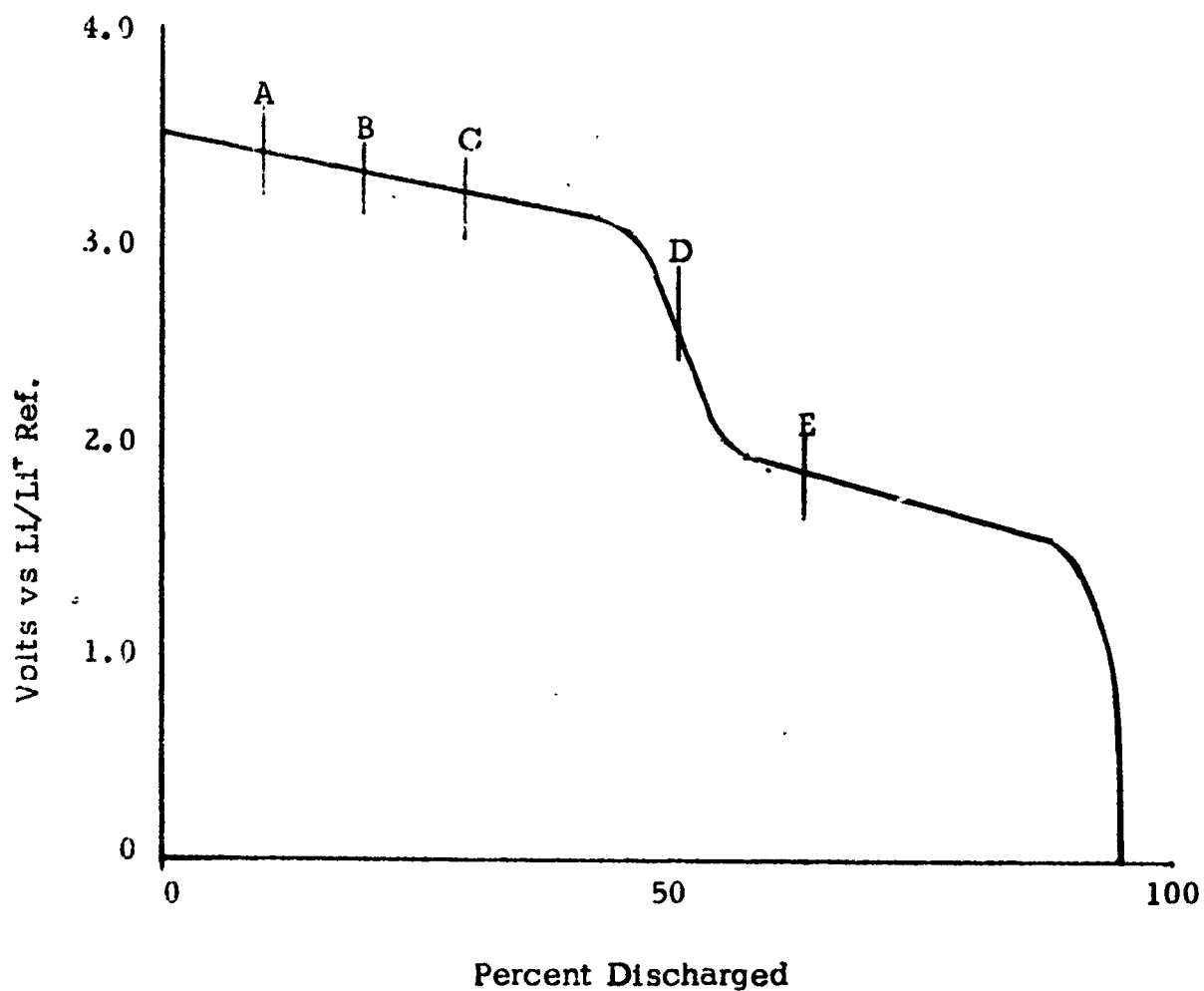


Figure 26



Kinetic Study -  $\text{CuF}_2$  Cathode  
Analysis of Reaction Products at  
Various Stages of Discharge



Results of X-Ray Analysis

	$\text{CuF}_2$	$\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	$\text{LiF}$	$\text{Cu}$	Graphite
Control	Present	Present	--	--	Present
A			Present	Present	"
B	< A	< A	> A	> A	"
C	< A	< B	> B	> B	"
D	< C	< C	> C	> C	"
E	< D	< D	> D	> D	"

Figure 27

# Typical Discharge Characteristic of Pressed Lithium Ribbon Anode

Electrolyte 1 Formal  $\text{LiClO}_4$  in Propylene Carbonate

Current density  $\text{ma cm}^{-2}$

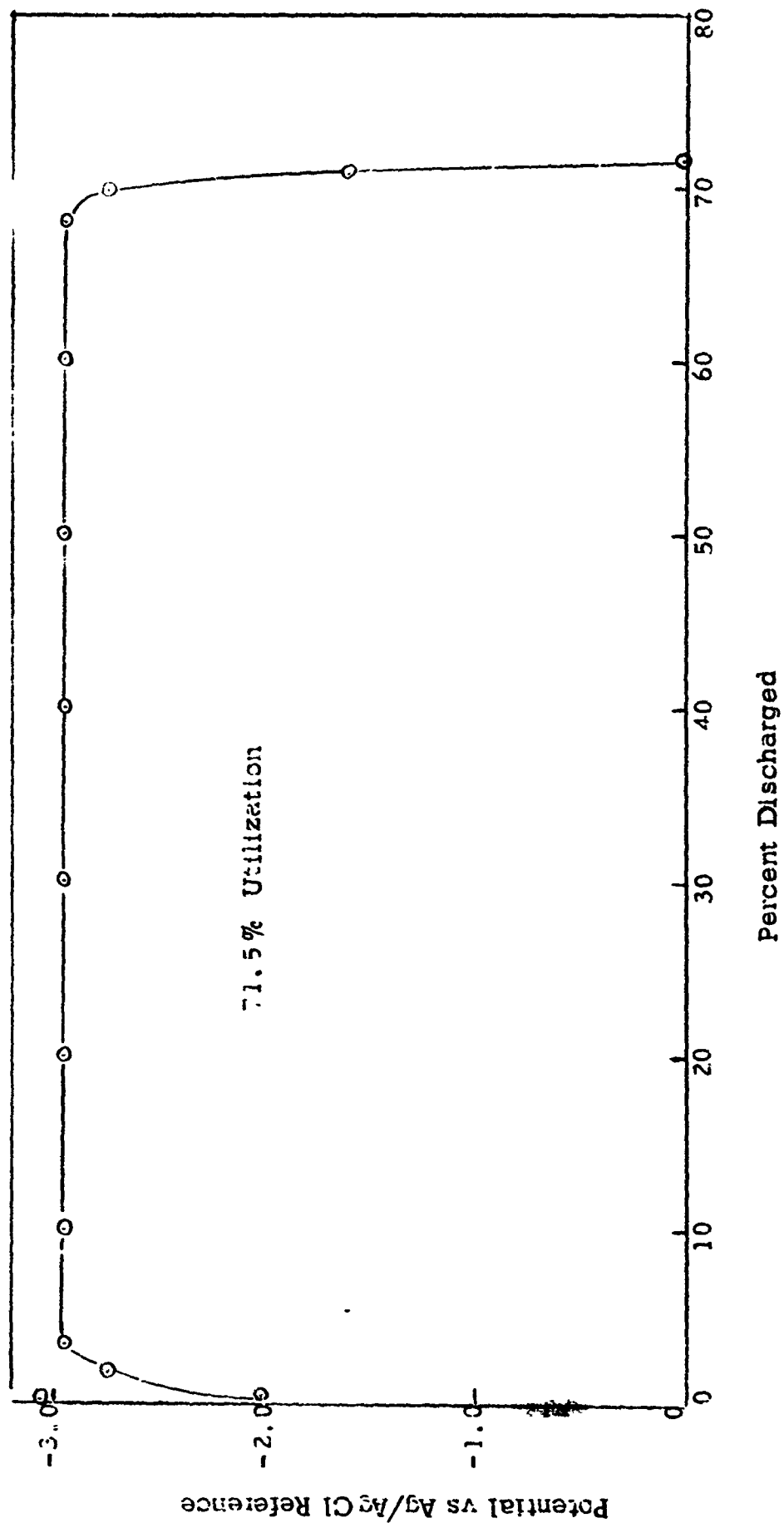


Figure 28